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treated mainly from a theoretical point of view; in the five succeeding chapters, the nature, properties, and testing of lubricants are dealt with; and the two final chapters are devoted to a description and discussion of the practical application of lubricants to machinery for the purpose of reducing friction and wear. In the last chapter, which has been written chiefly for engineers in charge of machinery, many points are again briefly discussed which have already been more fully treated in earlier portions of the work.

The descriptions of oil-testing machines in the chapter on the mechanical testing of lubricants are based almost entirely on published information; but, in the instructions for their manipulation, an endeavour has been made to state the conditions under which tests may be made for "oiliness" or for viscosity, much that has been written on the subject being unsound, owing to a want of knowledge concerning the conditions under which these two properties of lubricants are of active value.

For the theory of viscous lubrication we are indebted, firstly, to the experimental work carried out for the Institution of Mechanical Engineers by Mr. Beauchamp Tower, and secondly, to the theoretical explanation of Mr. Tower's results communicated to the Royal Society by Professor Osborne Reynolds, F.R.S. Without losing sight of the valuable work done by other investigators, amongst whom should be mentioned Professors Thurston and Goodman, also Mr. Veitch Wilson, who, as a manufacturer, has laboured for so many years to spread a correct knowledge of the nature and properties of lubricants among users, it is not too much to say that the work done by Mr. Beauchamp Tower and Professor Osborne Reynolds has been mainly instrumental in leading to the adoption of scientific methods of lubrication, and has enabled the part played by the viscosity of the lubricant to be clearly stated. An equally complete treatment of the theory of oiliness or greasiness is at present impossible; but the bearing

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Our best thanks are due to Mr. C. E. Wolff, B.Sc., for assistance in some of the mathematical portions of the work, to Mr. T. H. Adams for assisting in the experimental work, and to Messrs. H. R. Haigh, J. F. Ingleby, H. Jessop, Colin R. Strong, R. Weatherburn, and others to whom we are indebted for information, suggestions, or assistance in other ways.

L. ARCHBUTT.
R. M. DEELEY.

DERBY, *September* 1899

CONTENTS.

CHAPTER I.

FRICTION OF SOLIDS.

PAGE

Introductory, ... 1

Nature of Friction, ... 2

Circumstances which Influence Friction, . . 3

    Cohesion, ... 3

    Chemical and Physical Surface Actions, . . 4

Solid Lubricants, ... 5

Coefficient of Friction, ... 6

    Static and Kinetic Coefficients, ... 6

Solid Friction, ... 7

    Condition of Contact Surfaces, ... 7

    Rennie's Experiments, ... 7

    Friction and Speed, ... 8

    Theory of Solid Friction, ... 9

    Laws of Solid Friction, ... 10

    Effects of Speed, ... 10

Rolling Friction, ... 13

Cause of Heating, ... 14

CHAPTER II.

LIQUID FRICTION, OR VISCOSITY, AND PLASTIC FRICTION.

Introductory, ... 16

Nature of Viscosity, ... 16

Cohesion and Viscosity, ... 17

Viscous Flow and Lubrication, ... 17

Viscous Flow between Parallel Horizontal Planes having Differential Tangential Motion, ... 17

Viscous Flow under the Action of Gravity between Fixed Planes, ... 19

PAGE
Viscous Flow through Capillary Tubes, ... 22
Physical and Mechanical Viscosity, ... 23
Effects of Temperature and Pressure, ... 25
Conditions determining Steady Flow, ... 25
Energy of Flow through Capillary Tubes, ... 26
Correction for Energy of Flow, ... 27
Viscometer Proportions, ... 28
Inlet-End Resistance, ... 28
Plastic Friction, ... 29

CHAPTER III.

SUPERFICIAL TENSION.

Lubrication and Superficial Tension. 31
Lubricating Films, ... 31
Soap (Bubble) Films, ... 31
Wetting of Solid Surfaces, ... 32
Theory of Superficial Tension, ... 32
Molecular Attractions, ... 32
Intensity of Molecular Stresses, ... 33
Condition of Surface Molecules, ... 33
Liquid Interfaces, ... 34
Miscibility of Liquids, ... 34
Surface Tension of Solids, ... 35
Contact of Liquids and Solids, ... 36
Lubricating Films, ... 37
Oiliness, ... 37
Stability of Liquid Films, ... 38
Circumstances which modify Surface Tension, ... 39
Temperature, ... 39
Solubility, ... 39
Superficial Solubility, ... 40
Contamination of Liquid Surfaces, ... 40
Surface Energy, ... 41
Proportional to Surface Area, ... 41
Emulsions, ... 42
Cause of Wetting, ... 42
Capillarity, ... 42
Capillary Rise in Tubes, ... 42
Flow through Wicks, ... 43
Cohesion Figures, ... 44
Measurement of Surface Tension, ... 45
Tension of Films, ... 45
Rise in Capillary Tubes, ... 45

PAGE

easurement of Surface Tension—*continued.*
- Measurement by Film Tension, ... 46
- Measurement by Wetted Plate, ... 47

CHAPTER IV.

THE THEORY OF LUBRICATION.

ubrication and Friction, ... 49
- Lubrication of Surfaces, ... 49
- Objects of Lubrication, ... 49
- Theory of Lubrication, ... 50
- Frictional Losses, ... 51
- Conditions of Lubrication, ... 51

atic Lubrication, ... 51
- Friction of Thin Lubricating Films, ... 51
- Static Coefficient of Friction, ... 52
- Plastic Friction, ... 52
- Effects of Superficial Tension, ... 53

ow Speed Lubrication, ... 55
- Conditions of Lubrication, ... 55
- Metals for Bearing Surfaces, ... 56
- Influence of Viscosity, ... 56
- Coefficient of Friction at Low Speeds, ... 57
- Theory of Low Speed Lubrication, ... 62
- Lubrication with Plastic Solids, ... 63

igh Speed Lubrication, ... 64
- Lubricating Film, ... 64
- Lubrication of Plane Parallel Surfaces, ... 64
- Lubrication of Inclined Plane Surfaces, ... 69
- Lubrication of Cylindrical Surfaces, ... 72
- Effects of Load and Speed, ... 73
- Effects of Viscosity, ... 76
- Effects of Area, ... 79
- Alternating Pressures, ... 81

ear of Cylindrical Brasses, ... 81

nperfect Lubrication, ... 82

all and Roller Bearings, ... 83

CHAPTER V.

LUBRICANTS—THEIR SOURCES, PREPARATION, AND CHIEF PROPERTIES.

MINERAL OILS, ... 86
- **Sources,** 86
  - Petroleum, ... 86
  - Shale, ... 89

PAGE
Manufacture, ... 89
  Natural Oils, ... 92
  Reduced Oils, ... 92
  Distilled Oils, ‘Paraffin Oils,’ 92
  Russian Oils, ... 95
  Shale Oils, ... 96
Properties and Composition of Mineral Lubricating Oils, . 97

B. FIXED OILS AND FATS, ... 99
Sources, Composition, and General Properties, . . 99
  Rape (Colza) Oil, ... 102
  Black Sea Rape Oil. Ravison Oil, ... 106
  Olive Oil, ... 106
  Olive-Kernel Oil, ... 108
  Castor Oil, ... 108
  Palm Oil, ... 110
  Palm-Nut Oil, ... 110
  Coconut Oil, ... 110
  Tallow, ... 111
  Tallow Oil, ... 112
  Lard Oil, ... 112
  Neatsfoot Oil, ... 113
  Whale Oil, ... 113
  Sperm Oil. Arctic Sperm (Bottlenose) Oil, . . . 114
  Porpoise Jaw Oil, ... 115
  Dolphin (Blackfish) Jaw Oil. ‘Melon’ Oil, . . . 115

C. BLOWN OR THICKENED OILS, ... 116

D. ROSIN OIL, ... 119

E. LUBRICANTS CONTAINING SOAP. GREASES, . . 120
  Soap-thickened Oils, ... 120
  Soap-thickened Greases, ... 121
  Railway Wagon Grease, ... 123
  Rosin Grease, ... 124
  Screwing and Drilling Liquids, ... 125

CHAPTER VI.

PHYSICAL PROPERTIES AND METHODS OF EXAMINATION OF LUBRICANTS.

A. VISCOSITY AND VISCOMETRY, ... 126
Absolute Viscometry, ... 126
  Description of an Absolute Viscometer, ... 127
  Determination at 20° C. of the Viscosity of Water, . . 129
  Viscosities, at 20° C., of Mixtures of Glycerol and Water, . 130

PAGE

Commercial Viscometry, ... 137
- Redwood's Standard Viscometer, ... 138
- The Coleman-Archbutt Viscometer, ... 140
- Saybolt's Viscometer, ... 143
- Engler's Standard Viscometer, ... 144
- The Engler-Kunkler Viscometer, ... 145

The Expression of Viscosity Values, ... 147

The Standardizing of Commercial Viscometers, . . 148
- Results obtained with the Redwood Viscometer, . . 149
- " " " Coleman-Archbutt Viscometer, . 150

Rules for Determining, by means of a Standardized Viscometer, the Viscosity of a Lubricating Oil in Absolute Measure at any desired Temperature, . 153

Apparatus for Determining the Consistence of Solid Fats and Greases, ... 162
- Kissling's Apparatus, ... 162
- Kunkler's Apparatus, ... 162

B. SPECIFIC GRAVITY AND DENSITY, ... 164

Determination of Specific Gravity, ... 164
- Bottle Method, ... 165
- Sprengel Tube Method, ... 166
- Westphal Balance Method, ... 167
- Hydrometer Method, ... 169
- Alcohol Method, ... 170

Reduction to the Vacuum, ... 171

Change of Standard (Determination of Density), . . 172

Alteration in the Densities of Lubricating Oils produced by Change of Temperature, ... 173

C. FLASHING-POINT, ... 178

Determination of the Flashing-Point, ... 179
- "Open-Test." Flashing- and Firing-Point, ... 179
- "Closed Test," 179
- The Pensky-Martens Test Apparatus, ... 179
- Gray's Test Apparatus, ... 181

D. VOLATILITY, ... 183

Determination of Volatility, ... 183
- Archbutt's Vapourimeter, ... 184

E. SETTING-POINT OR COLD-TEST OF LUBRICATING OILS, ... 187

Determination of the Setting-Point, ... 188
- The Scotch Method, ... 188
- Archbutt's Method, ... 188
- Hofmeister's Method, ... 189

PAGE
Determination of the Setting Point—continued.
Schultz's Method, ... 190
Tagliabue's Standard Oil-Freezer, ... 191
MELTING POINTS OF FATS AND LUBRICATING GREASES, . . . 192
Melting and Solidifying Points of Fatty Acids, . . 192
Preparation of the Substance, ... 193
Determination of Melting and Solidifying Points, . . 193
[illegible] Method, . . . 193
[illegible] Method for Greases, . . . 193
Capillary Tube Method, . . 194
Bensemann's Method, . . 195
[illegible] Method, ... 195
[illegible] Method, ... 196
Dalican's Titer Test, ... 196
REFRACTION TEST, ... 198
Amagat and Jean's Oleo-Refractometer, . . . 198
COLOUR AND APPEARANCE, ... 200

CHAPTER VII.

CHEMICAL PROPERTIES AND METHODS OF EXAMINATION OF LUBRICANTS.

FREE ACID OR ACIDITY, ... 201
Determination of the Amount of the Free Acid in Oils, . . 201
Effect of Free Fatty Acids in Lubricants, . . . 204
Determination of Acidity, . . . 206
[illegible] Expressing Acidity, . . . 206
[illegible] in a fluid Oil, . . . 207
Solid Fat, . . . 207
dark coloured Oils, . . 207
[illegible] Acid, ... 208
[illegible] free fatty and resin Acids, . 208
Amount of Free Acid Permissible in Lubricants, . . 208
[illegible] Small Quantities of Oil, . . . 209
DETERMINATION OF SAPONIFIABLE AND UNSAPONIFIABLE OIL, . . . 209
Detection of Fatty Oil in Mineral Oil, . . 209
Mineral Oil in Fatty Oil, . . . 210
THE SAPONIFICATION VALUE, . . . 210
Meaning and Use of this Value, . . . 210
Determination of the Saponification Value, . . . 211
Explanation of Terms . . 214

PAGE

D. APPROXIMATE ANALYSIS OF MIXED LUBRICATING OILS, ... 214

E. ESTIMATION OF TOTAL UNSAPONIFIABLE MATTER, ... 215

General Method for the determination of Unsaponifiable Matter in an Easily saponifiable oil, fat, or fluid wax, 215

Modification in presence of much Mineral Oil, . . 217

Modification in presence of Wool Fat, . . . 217

Modification in presence of Beeswax, . . . 218

Estimation of Small Quantities of Saponifiable Matter in Mineral Oils, ... 219

F. COMPOSITION AND IDENTIFICATION OF UNSAPONIFIABLE MATTERS, ... 219

Hydrocarbons (Mineral Oil, Rosin Oil, Vaseline, etc.), . 219

Wax Alcohols from Sperm Oil, Wool Fat, etc., . . 221

Cholesterol and Phytosterol, ... 222

Unsaponified Oil or Fat, and Soap, ... 223

G. ESTIMATION AND IDENTIFICATION OF THE SAPONIFIABLE OIL IN MIXED OILS, . . 224

H. INSOLUBLE FATTY ACIDS (HEHNER VALUE), . 226

Determination of the Hehner Value, . . . 226

Qualitative Preparation of Insoluble Fatty and Resin Acids, ... 227

. ESTIMATION OF ROSIN (COLOPHONY), ... 227

J. VOLATILE FATTY ACIDS (REICHERT AND REICHERT-MEISSL VALUES), ... 229

The Reichert Process, ... 229

The Reichert-Meissl Process, ... 230

K. ACETYLATION TEST (THE ACETYL VALUE), . . 231

Acetylation of Alcohols, ... 231

Analysis of Mixtures containing Sperm Oil or Wool Fat and Mineral Oil, ... 233

Acetylation of Hydroxylated Fatty Acids and Glycerides, 235

Determination of the Acetyl Value, ... 235

Benedikt's Method, ... 236

Lewkowitsch's Method, ... 238

L. THE IODINE VALUE, ... 240

Meaning and Use of this Value, ... 240

Determination of the Iodine Value, ... 241

Hübl's Process, ... 241

Wijs's Process, ... 244

M. HEHNER'S BROMINE THERMAL TEST, . . 247

PAGE

N. MAUMENÉ'S THERMAL TEST, ... 250
  Specific Temperature Reaction, ... 253

O. OXIDATION AND GUMMING OF LUBRICATING OILS, 254
  Fixed Oils, ... 254
    Watch-glass Test, ... 255
    Film Test, ... 255
    Livache's Test, ... 256
    Bishop's Test, ... 258
    Oxygen Absorption Test, ... 260
  Mineral Oils, ... 261

P. SPONTANEOUS COMBUSTION OF OILY MATERIALS, 268
    Albright and Clark's Apparatus, ... 269
    Mackey's Cloth-Oil Tester, ... 270

Q. DETECTION AND ESTIMATION OF ARACHIS OIL IN OLIVE OIL, ... 273

R. COLOUR REACTIONS, ... 277
    Reactions of Cottonseed Oil, ... 277
    Reaction of Sesamé Oil, ... 280
    Reactions of Cholesterol and Phytosterol, ... 281
    Detection of Rosin Oil, ... 282
    Detection of Resin Acids, ... 284

S. DETECTION AND ESTIMATION OF ROSIN OIL IN MINERAL OIL, ... 284
    The Liebermann-Storch Colour Test (See under R).
    The Acetone Test, ... 284
    Finkener's Test, ... 285
    Polarimetric Test, ... 285
    Estimation of Rosin Oil by Storch's Method, . . . 285
    „ „ „ M'Ilhiney's Method, . . . 286

T. ESTIMATION OF PARAFFIN IN MINERAL OILS, . 287

U. ASPHALT AND RESIN IN MINERAL OILS, . . 288

V. CAOUTCHOUC IN MINERAL OILS, ... 290

W. DETECTION OF SOAP AND INORGANIC SUBSTANCES IN MINERAL OILS AND GREASES, ... 291

X. DETERMINATION OF ASH, ... 292

Y. DETECTION OF NITROBENZENE AND NITRONAPHTHALENE, ... 292

Z. DETECTION AND ESTIMATION OF WATER, . . 293

CHAPTER VIII.

THE SYSTEMATIC TESTING OF LUBRICANTS BY PHYSICAL AND CHEMICAL METHODS.

PAGE
. **UNDESCRIBED OILS,** 295
. **MINERAL OILS,** 296
. **FIXED OILS AND FATS,** 300
  Rape Oil, ... 301
  Olive Oil, ... 305
  Castor Oil, ... 308
  Palm Oil, ... 309
  Palmnut and Coconut Oils, ... 309
  Tallow, ... 310
  Tallow Oil, ... 311
  Lard Oil, ... 312
  Neatsfoot Oil, ... 312
  Whale Oil, ... 313
  Sperm Oil, ... 313
  Porpoise and Dolphin Jaw Oils, ... 315
. **BLOWN OR THICKENED OILS,** 315
. **MIXED LUBRICANTS,** 317
  Mixed Oils and Greases free from Soap, ... 317
  Mixed Oils and Greases containing Soap, ... 317

CHAPTER IX.

THE MECHANICAL TESTING OF LUBRICANTS.

ıtroductory, ... 319
bjects of Mechanical Testing, ... 320
esign of Oil-Testing Machines, ... 320
ylindrical or Drum Machines, ... 322
  Thurston's Oil-Testing Machines, ... 322
  Methods of Working Thurston's Machines, ... 327
  Ingham and Stapfer's Oil-Testing Machine, ... 330
  Ashcroft's Oil-Testing Machine, ... 330
  Stroudley's Oil-Testing Machine, ... 331
  Beauchamp Tower's Experimental Oil-Testing Machine, . 333
  Goodman's Oil-Testing Machine, ... 334
isc and Collar Machines, ... 335
  Suitability for Oil-Testing, ... 335
  MacNaught's Oil-Testing Machine, ... 336
  Woodbury's Oil-Testing Machine, ... 337
  Deprez and Napoli's Oil-Testing Machine, ... 338
  Tower's Disc and Collar Oil-Testing Machines, . . . 338
  Bailey's Pendulum Oil-Testing Machine, ... 340

CHAPTER X.

THE DESIGN AND LUBRICATION OF BEARINGS.

PAGE
Forms of Bearing Surfaces, ... 341
Nature of Surfaces in Contact, ... 341
Protection of Bearing Surfaces, ... 342
Materials and Lubricants for Bearing Surfaces, ... 342
Exposed Rubbing Surfaces, ... 343
Hardening of Bearing Surfaces, ... 343
  Hard Steel Surfaces, ... 343
  Burnished Bearings, ... 344
  Case-hardened Iron and Mild Steel Surfaces, . . . 344
  Chilled Cast-Iron Surfaces, ... 344
  Estimation of Hardness, ... 345
Materials for Bearings, ... 347
  Cast-Iron, ... 347
  Bronze, ... 347
  White-Metal, ... 349
  Aluminium, ... 353
  Wood and Hide, ... 353
  Other Non-Metallic Materials, ... 354
The Lubrication of Bearings, ... 354
  Friction and Speed, ... 354
  Slow-Speed Lubrication, ... 355
  High-Speed Lubrication, ... 355
  "Perfect" Lubrication, ... 356
  Oil-Spray Chambers, ... 358
  Oil-Pressure Film, ... 358
  Positions of Oil-Ways, ... 359
  Pad Lubrication, ... 361
  Bath Lubrication, ... 362
  Force-Pump Lubrication, ... 362
Heating of Lubricating Films, ... 363
Admissible Loads on Bearings, ... 364
Fit of Bearings, ... 366
  Bedding of Brasses, ... 366
  Workmanship, ... 368
  Wear of Bearings, ... 368
Forms of Cylindrical Bearings, ... 369
  Bush Bearings, ... 369
  Watch and Clock Bearings, ... 369
  Pedestal Bearings, ... 370
  Axle-Boxes, ... 373
  Grease-Boxes, ... 375
  Spindle Bearings, ... 375
  Loose Pulleys, ... 376

PAGE
Variable Load Bearings, ... 377
Pins with Reciprocating Motion, ... 379
Plane Surface Bearings, ... 379
Loading of Plane-Surface Bearings, ... 379
Slide-Blocks, ... 379
Collar Bearings, ... 380
Pivot Bearings, ... 381
Piston Rod Packings, ... 382
Rolling Contact Bearings, ... 382
Ball Bearings, ... 382
Roller Bearings, ... 384
Methods of Applying Lubricants, ... 384
Efficient Lubrication, ... 384
Pump Circulation, ... 385
Siphon and Drop-Feed Lubrication, ... 385
Grease Cups, ... 386
Steam Cylinder Lubricators, ... 386
Design of Cylinders, ... 391

CHAPTER XI.

THE LUBRICATION OF MACHINERY.

Genuineness of Lubricants, ... 393
Simple Tests, ... 394
Qualities and Properties of Lubricants, ... 395
Acidity, ... 395
Gumming, ... 395
Freezing, ... 396
Greasiness and Oiliness, ... 396
Viscosity, ... 397
Staining, ... 398
Blended Lubricants, ... 399
Mixed or Blended Oils, ... 399
Fats and Greases, ... 401
Clarification of Lubricants, ... 402
Oil Filters, ... 402
Grit, etc., in Oil, ... 404
Straining of Oil, ... 404
Lubrication of Bearing Surfaces, ... 405
Lubricants for Low Speeds, ... 405
Lubricants for Moderate Speeds, ... 406
Lubricants for High Speeds, ... 407
Lubricants for Miscellaneous Machines, ... 407
Hydraulic Lubricants, ... 408
Solid Lubricants, ... 409

PAGE
Lubricants for Nuts, Keys, etc., ... 409
Lubricants for Boiler Fittings, ... 409
Selection of Lubricants, ... 410
Cost and Efficiency of Lubricants, ... 410
Management of Machinery, ... 411
Cleanliness, ... 411
Starting of New Machinery, ... 412
Methodical Habits of Lubrication, ... 413
Examinations of Bearings, ... 414
Examination Book, ... 415
Preservation of Machinery not in Regular Use, ... 415
Grease for Protecting Polished Surfaces, ... 416
Overheating of Bearings, ... 416
Efficiency of Lubricants, ... 418
Steam Cylinder and Valve Lubrication, ... 419
Imperfect Nature of, ... 419
Evaporation of Oil, ... 419
Decomposition of Lubricants, ... 420
Application of Cylinder and Valve Lubricants, ... 421
Lubrication of Cutting Tools, ... 422
Frictional Losses, ... 423
Magnitude of Losses, ... 423
The Efficiency of Mechanism, ... 424
Electrical Transmission of Power, ... 424
Economical Lubrication, ... 424
Indicating of Motors, ... 425
Estimation of Cost of Frictional Losses, ... 425
Estimation of Losses due to Wear, ... 426
Oil-Cans, Feeders, etc., ... 427

Index, ... 428

LIST OF TABLES.

TABLE PAGE
I. Friction between Metal Surfaces, ... 8
II. Relative Coefficients of Friction of Leather on Iron, ... 9
III. Friction of Railway Brakes, . . . 11
IV. Friction of Wheel on Rail, . . . 11
V. Coefficient of Friction at a Speed of 7·8 Feet per Minute, ... 57
VI. Relative Coefficients of Friction at Low Speeds, 58
VII. Relative Coefficients of Friction at Moderate Speeds, ... 58
VIII. Changes in Value of Coefficient of Friction with Increasing Speed, ... 61
IX. Frictional Resistance of Pivots (*Tower*), . . 70
X. Frictional Resistance with Bath Lubrication (*Tower*), ... 74
XI. Coefficient of Friction at Different Speeds (*Goodman*), ... 75
XII. Coefficient of Friction at Various Speeds and Temperatures (*Tower*), ... 77
XIII. Oil-Bath Low-Speed Friction (*Goodman*), . . 79
XIV. Oil-Bath Friction with Varying Loads (*Goodman*), 80
XV. Influence of Method of Lubrication and Contact Area upon Frictional Resistance, . 82
XVI. Frictional Resistance of "Rudge" Ball-Bearing-Pale American Oil, ... 83
XVII. Frictional Resistance of "Rudge" Ball-bearing-White "Neutral" Oil, ... 84
XVIII. Fractional Distillates from Russian Petroleum Residuum, ... 96
XIX. Fatty Acids occurring in Lubricating Oils, . 102
XX. Properties of Indian Rape Oil, ... 103
XXI. Effect of Refining Rape Oil by Thénard's Method, ... 104
XXII. Properties of Black Sea Rape Oil, . . . 107
XXIII. Proportions of Mineral Spirit and Mineral Oils miscible with Castor Oil, ... 110

TABLE PAGE
XXIV. RATIOS OF VISCOSITY OF SPERM, OLIVE, AND RAPE OILS, 115
XXV. PROPERTIES OF PORPOISE AND DOLPHIN JAW OILS, . 116
XXVI. CHEMICAL CHANGES PRODUCED BY BLOWING OILS, . 118
XXVII. LIME, SODA, AND LEAD SOAP GREASES, . . 122
XXVIII. FORMULÆ FOR RAILWAY WAGON GREASE, . . 123
XXIX. VISCOSITIES OF MIXTURES OF GLYCEROL AND WATER, 131–133
XXX. " " " " 134–137
XXXI. GLYCEROL AND WATER MIXTURES FOR STANDARDIZING THE REDWOOD VISCOMETER, . . . 148
XXXII. RESULTS OBTAINED BY STANDARDIZING THE REDWOOD VISCOMETER, ... 149
XXXIII. RESULTS OBTAINED BY STANDARDIZING THE COLEMAN VISCOMETER, ... 150
XXXIV.-XXXVI. VISCOSITIES OF OILS IN DYNES PER SQ. CM., 154–159
XXXVII. VARIATIONS IN WESTPHAL BALANCE RIDERS, . 168
XXXVIII. FORMULÆ FOR CONVERTING HYDROMETER DEGREES TO SPECIFIC GRAVITIES, ... 171
XXXIX. CORRECTION FOR REDUCTION OF SPECIFIC GRAVITY TO A VACUUM, ... 172
XL. DENSITY OF WATER AT 4° C. TO 100° C., . . 174
XLI. SHOWING THE ALTERATION IN DENSITY OF LUBRICATING OILS CAUSED BY RISE OF TEMPERATURE, . 175
XLII. SPECIFIC GRAVITIES AT 60° F. (15·5° C.) OF FIXED OILS, ETC., ... 176
XLIII. SPECIFIC GRAVITIES AT $\frac{100^\circ}{100^\circ}$ C. OF SOME MIXED FATTY ACIDS, ... 177
XLIV. SPECIFIC GRAVITIES AT $\frac{100^\circ}{100^\circ}$ C. OF SOME MIXED ALCOHOLS, ... 177
XLV. SPECIFIC GRAVITY AT 60° F. (15·5° C.) OF MINERAL LUBRICATING OILS, ETC., ... 177
XLVI. EFFECT OF VARYING THE VOLUME OF OIL IN DETERMINING THE FLASHING-POINT, . . . 181
XLVII. FLASHING-POINTS AND VOLATILITY COMPARED, . 186
XLVIII. SALINE FREEZING SOLUTIONS, ... 189
XLIX. SETTING-POINTS OF SOME VEGETABLE AND ANIMAL OILS, ... 191
L. SETTING-POINTS OF MINERAL LUBRICATING OILS, . 192
LI. MELTING-POINTS OF SOME FATS, WAXES, ETC., . 196
LII. MELTING- AND SOLIDIFYING-POINTS OF MIXED FATTY ACIDS, ... 197
LIII. REFRACTIVE INDICES, ... 198

TABLE PAGE

LIV. Tests of Oils with Amagat and Jean's Oleo-Refractometer, ... 199

LV. Free Acid in Olive Oils, ... 202

LVI., LVII. Free Acid in Tallows, ... 203

LVIII. Saponification Values of Oils, Fats, and Waxes, 213

LIX. Properties of Cholesterol, Isocholesterol, and Phytosterol, ... 222

LX. Percentage of Unsaponifiable Matter obtained from Fixed Oils, Fats, and Waxes, . . 223

LXI. Properties of the Mixed Alcohols, etc., obtained from Waxes, ... 224

LXII. Hehner Values, ... 228

LXIII. Reichert and Reichert-Meissl Values, . . 232

LXIV. Results of the Acetylation of Alcohols, . . 234

LXV. Acetyl Values of Oils (*Benedikt*), . . . 237

LXVI. " " " (*Lewkowitsch*) . . 239

LXVII. Iodine Values determined by Hübl's and Wijs's Methods, ... 244

LXVIII. Hübl Iodine Values of Fixed Oils, Fats, and Waxes, and of their Mixed Fatty Acids, . 245

LXIX. Hübl Iodine Values of Miscellaneous Substances, 246

LXX., LXXI. Bromine Thermal Values and Calculated Iodine Values of Rape, Olive, and Linseed Oils and Tallow, ... 249

LXXII. Influence of the Strength of Acid on the Maumené Test, ... 250

LXXIII. Maumené Thermal Values, ... 252

LXXIV. Influence of the Strength of Acid on the "Specific Temperature Reaction," . . 253

LXXV. Relation between the Iodine Value of Rape Oil and the Maumené and Bromine Thermal Values, ... 254

LXXVI. Effect of Exposing some Fixed Oils in Thin Films to Air at 50° C., ... 256

LXXVII. Increase of Weight of Oils by Oxidation (*Livache*), 257

LXXVIII.-LXXX. Changes of Weight of Oils by Oxidation (*Bishop*), ... 258, 259

LXXXI., LXXXII. Volumes of Oxygen absorbed by Oils, . 261

LXXXIII.-LXXXV. Changes undergone by Mineral Oils when Heated in thin layers exposed to Air, 262-267

LXXXVI. Results obtained with Mackey's Cloth-Oil Tester, 271

LXXXVII. Temperatures at which Crystals form in Renard's process for Arachis Oil, . . 274

TABLE PAGE
LXXXVIII. Correction for Solubility of Arachis Acids in 90% Alcohol, ... 275
LXXXIX. Results of Analysis of Mixtures of Olive Oil and Arachis Oil, ... 276
XC. Absolute Viscosities of Oils for various purposes, ... 298
XCI. Physical and Chemical Constants of Fixed Oils used for Lubrication, ... 302, 303
XCII. Properties of Southern and Arctic Sperm Oils, 314
XCIII. Relative Hardness of Metals, ... 345
XCIV. Percentage Composition of Machine Bearings, . 349
XCV. Percentage Composition of White-Metals, . 351
XCVI. Admissible Loads on Bearings, ... 367

MEANING OF THE SYMBOLS EMPLOYED IN THIS WORK.

A.—*Area.*
a *and* l.—*Dimension in the direction of motion.*
b.—*Dimension at right angles to direction of motion.*
c.—*A constant.*
F.—*Total resistance.*
f.—*Resistance per unit of area.*
g.—*Force of gravity.*
H.—*Unit of heat.*
h.—*Head of liquid.*
k.—*A constant.*
N.—*Revolutions per minute.*
P.—*Total pressure.*
p.—*Pressure on unit area.*
T.—*Force of tension or compression.*
r.—*Radius or distance from a centre line.*
r_0.—*Radius of a tube or cylinder, or half the distance separating two planes.*
t.—*Time.*
V.—*Volume.*
v.—*Velocity.*
v_1.—*Maximum velocity.*
$\bar{v}$.—*Mean velocity.*
W *and* w.—*Weight or load.*
η.—*Viscosity.*
μ.—*Static coefficient of friction.*
μ_1.—*Kinetic coefficient of friction.*
π.—*Ratio of circumference to radius.*
τ.—*Thickness.*
d.—*Relative density.*
σ.—*Value analogous to density.*

LUBRICATION AND LUBRICANTS.

CHAPTER I.

FRICTION OF SOLIDS.

Introductory.—The object of mechanism of all kinds is the control or utilization of energy for the purpose of doing useful work. Owing, however, to the necessary imperfections of our methods, a large part of the energy applied is wasted in various ways; mainly, in overcoming the resistance to relative motion offered by the opposing surfaces of the machines themselves.

The least force properly applied to a perfect machine at rest should set it in motion, and, owing to the inertia of its parts, such a machine once set in motion, but not doing work, should continue to move with uniform velocity; but there are causes which operate to arrest motion, firstly, the inertia and frictional resistance of the air; secondly, the friction between the rubbing surfaces of the machine; and thirdly, induced electrical currents. The frictional resistance of the air may be reduced by shaping the moving surfaces of the machine so as to oppose the least surface to its action; with the electrical resistances we are not here concerned. The most serious resistance to the motion of heavy machinery is the friction between the opposing surfaces, and it is in order to reduce this friction to a minimum that lubrication is resorted to.

In some cases the frictional resistance between opposing surfaces is utilized as a means of transmitting motion from one portion of a machine to another, or from machine to machine. Friction clutches and belt or rope gearing may be instanced as cases in point. Here the object is to make the frictional resistance as great as possible, so that the opposing surfaces may not slip. Such devices are, however, beyond the scope of this work, for, although friction surfaces are often lubricated to a certain extent, the lubricant is applied to prevent the surfaces from seizing, and not to reduce friction. There are also instances in which lubrication is resorted to chiefly in order to reduce the wear of the friction surfaces, and this may be of such importance that the loss of energy by friction becomes quite a secondary consideration.

Lubrication is effected by interposing between the friction surfaces films of liquid or soft solid substances which decrease the friction. Such substances are called lubricants. The physical properties upon which their lubricating powers depend will be considered at a later stage; for the present we shall confine our remarks to a discussion of the nature and laws of so-called solid friction, *i.e.*, the friction between clean solid surfaces. Such surfaces are seldom chemically clean; but the contaminating films do not affect the laws of solid friction, they only determine the degree of resistance.

Friction is not merely a resistance to the relative motion of solid surfaces. The changes of shape undergone by solids when under stress, as well as the movements of liquids, are opposed by internal friction, which, in these cases, is of quite a different nature, and obeys different laws to the friction between opposed surfaces. Other chapters will, therefore, be devoted to the consideration of liquid friction, whilst in the present one the phenomena presented by the friction between solid surfaces only will be discussed.

Nature of Friction.—When two solid surfaces are pressed firmly together they cannot be moved relatively to each other without the exercise of considerable force; and when, by a sufficient effort, the surfaces have commenced sliding against each other, the resistance to be overcome in order to keep them in relative motion, though it may be either greater or less than was required to start them from a state of rest, has at all speeds a considerable retarding effect, and is called the friction between the surfaces. The frictional resistance varies greatly between different surfaces and materials, being least between hard and polished, and greatest between soft and rough surfaces. Between leather and coarse sandstone, for example, its value is very considerable, and it is owing to this fact that we are enabled to stand and walk in such perfect security on ordinary ground. Between leather and ice there is very much less friction. Walking on ice is, consequently, less secure than walking on the ground, and progression is more safely and easily effected by skating or sliding.

In the sliding or rolling of solids against each other friction owes its existence almost entirely to the roughness or unevenness of the surfaces in contact. Even apparently smooth surfaces are not free from minute elevations and depressions which interlock when such surfaces are pressed together. Motion can then only result either by the passage of one set of inequalities over the other, or by the forcible breaking off of projecting parts. When this takes place the surfaces may be continuously abraded, for it does not follow that they will be rubbed smooth by the friction.

Friction between surfaces of unequal hardness results in the more or less rapid abrasion of the softer surface, the harder surface suffering very slightly unless particles removed from it, or derived from extraneous sources, become embedded in the softer surface and act as graving tools. This is what occurs in the process known to mechanics as 'lapping,' in which emery or some other very hard substance is pressed into the surface of a soft metal, such as lead, which merely acts as a holder for the cutting material.

Friction may be greatly diminished by making the contact surfaces very smooth and of exceedingly hard materials. Absolutely smooth surfaces cannot be produced, even the most perfectly polished surfaces being more or less rough.

Rolling friction is of much the same nature as sliding friction. Upon perfectly plane surfaces the friction of rolling would be *nil*, but, as has just been pointed out, such surfaces cannot be produced, and inequalities remain which interlock and form obstacles to free motion. Moreover, pressure causes more or less deformation, both of the plane surface and of the face of the rollers, so that contact takes place not upon a line but upon a more or less broad strip, and as the roller moves along, fresh portions of the surfaces become distorted and some sliding friction occurs. Nevertheless, for the same load, much less resistance is offered to motion by rolling friction than by sliding friction. A block of stone, which would require the exertion of great force to push or drag it over the ground, can be moved with comparative ease upon wooden rollers. Vehicles are, for the same reason, provided with wheels; and, of late years, the substitution of rolling for sliding friction has been extensively applied in the roller and ball bearings of electro-motors, tram-cars, cycles, churns, clocks, astronomical telescopes, and many other machines and instruments where the pressure upon the surfaces is comparatively light. With this kind of friction, substances such as indiarubber, in the form of wheel tires for example, may be used to roll over comparatively rough surfaces without much loss of energy, the elasticity of the one surface enabling it to change its form to suit the inequalities of the ground.

Circumstances which Influence Friction.—*Cohesion.*—A cause of friction remains to be considered which is aggravated rather than diminished by our efforts to produce smooth surfaces. The more perfect the surfaces, the more closely will they be brought into contact, and at very small distances molecular forces come into play which cause very true surfaces to adhere strongly and thereby resist sliding impulses. Two pieces of plate-glass, for instance, carefully cleaned from dust, may, if placed upon one another and pressed together with a sliding motion, be caused to adhere * so strongly that

---

* A distinction is sometimes drawn between adhesion and cohesion which is not warranted by the facts. See Tait; *Properties of Matter*. 1st edition, p. 225.

[illegible] may be lifted [illegible] a vertical position by means of a [illegible] indeed a skilled workman can [illegible] that they cannot again be separated [illegible] the points of contact having become practically [illegible] together. In like manner pieces of marble, upon which [illegible] have been worked with great care, adhere when pressed together [illegible] their cohesion may be so great that [illegible] masses may remain suspended in virtue of their mutual [illegible] attraction. [illegible] surfaces of copper [illegible] when pressed together [illegible] early in the [illegible] one on another, [illegible] showed, more [illegible] similar [illegible]

In such [illegible] as have been [illegible] the materials may generally be [illegible] two surfaces of lead which have been freshly scraped [illegible] pressed together with a screwing motion, will [illegible] as firmly as if they formed one mass. In other words [illegible] the materials [illegible] welding. Prof. Walthere Spring has shown that [illegible] most metals if subjected to sufficient pressure may be [illegible] and even alloys of two or more [illegible] metals may be thus produced.* The pressure required is very much greater with a hard metal, such as aluminium, than with a soft metal like lead, but all the metals experimented upon were found to weld at ordinary temperatures if sufficiently compressed.

[illegible]—Not only do metals when brought into close contact adhere strongly; their surface atoms or molecules actually diffuse into each other at ordinary temperatures. Prof. Roberts-Austen, referring to his investigations on this subject, writes: "The continuation of these experiments has led to the recognition of the remarkable fact that diffusion of metals can readily be measured not only in molten but in solid metals. It is certainly remarkable that gold—placed at the bottom of a cylinder of lead 3 inches high, and heated to only 200° C. or 400° F., which is far below its melting point, and while it is to all appearance solid—will have diffused to the top in notable quantities by the end of three days. . . . The experiments summarized have already lead to the recognition of the undoubted fact that it is possible actually to observe and measure the migration of the constituent atoms in a metal or alloy at the ordinary temperature." All exposed surfaces are liable to undergo change, owing to the chemical action of gases contained in the atmosphere and other causes; and the films of oxide, sulphide, grease, oil, etc., produced in this way modify the effects of cohesion. Thus, in the experiment with lead described above, unless the metallic surfaces are perfectly bright and untarnished, though they will cohere

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* Roberts-Austen; *Introduction to the Study of Metallurgy.* 3rd edition, p. 65.

strongly, they will not weld in the cold. Of course, the pressures used in Prof. Walthère Spring's experiments were far greater than are brought to bear upon ordinary bearings; but, as shewn above, cohesion commences between very smooth surfaces under very moderate pressures, and the increased friction thus set up rapidly causes the bearings to become heated. This reduces the pressure at which welding takes place, and as soon as the welding pressure coincides with that to which the bearing is subject, the metallic surfaces seize or abrade each other. Contamination films, except when the pressures are small and the rate of motion slow, are soon rubbed out. Under all circumstances, therefore, where the heat due to friction can accumulate, that is where it is not produced so slowly or in such small amount as to be conducted away as rapidly as formed, a solid or fluid lubricant must be interposed between the adjacent surfaces, if only to keep them sufficiently apart to prevent friction due to cohesion.

Although the chemically clean and true surfaces of such metals as lead, tin, or wrought-iron will not slide upon each other without seizing, cast-iron may with impunity move in contact with wrought-iron and steel, even when the surfaces are clean and the pressures moderately great; indeed, dissimilar metals always work better and with greater ease upon each other than do similar ones. The foregoing statement may seem to conflict with results which have been obtained in measuring the frictional resistance between similar metals. In every case, however, when this has been done between 'tough' metals, there is reason to suppose that the surfaces were not chemically clean; for, although experiments have been made both with and without lubricants, in most cases the condition of the unlubricated surfaces has been described as 'unctuous.'

The friction between most so-called 'unlubricated' metallic surfaces is, therefore, not a case of true friction between pure metals, but between surfaces contaminated by atmospheric agencies, by grease, etc. from the material with which the surfaces were wiped, or by chemically formed films, such as oxides, sulphides, etc. Under moderate pressures such films prevent the actual adhesion of metal to metal, if the rate of motion be not too high and the action not too prolonged. This must be clearly borne in mind, otherwise what is known as 'solid friction' will not appear in its true light. However, so far as is at present known, the laws of friction between contaminated surfaces, and such clean surfaces *as will run together*, are identical. A contaminated surface is not to be regarded as one that is necessarily defiled, but merely one that has foreign matter on it.

Solid lubricants are all substances which, although they may often be welded into more or less solid masses by pressure, oppose comparatively small resistances to 'shear,' or to the movement of smooth surfaces in contact with them. They differ in their action from fats and greases, inasmuch as the latter melt and form oils at comparatively low temperatures, whilst the solids referred to maintain their condition unaltered between the surfaces, and prevent seizing or tearing even when the frictional resistances raise the temperature of the bearings very considerably. The coefficient of friction of such lubricants is, however, high, and when economy of power is of consequence, liquid lubricants and a sufficiently large bearing surface should be used wherever practicable.

Coefficient of Friction.—The relationship borne by the *frictional resistance* to the *load* or *force* pressing the surfaces together has been the subject of much speculation and discussion, and although numerous experimental researches have been carried out, such as those of Amontons, Coulomb, Vince, Rennie, Morin, Kimball, and others, there has always been much conflict of opinion. From what has been stated concerning the action which solid surfaces in close contact have upon each other, it will be clear that, although it may be possible to formulate somewhat general laws of solid friction, such laws cannot be expected to hold good under extremes of pressure or speed; and they will be affected to some extent by the nature of the materials in contact and the surface conditions.

The apparatus used by General Morin for measuring the friction between surfaces consisted of a loaded box (resting on a horizontal slide) from which a cord passed over a pulley and carried a smaller suspended box, which could be loaded with any desired weight. Both slider and slide could, after each set of experiments, be replaced by others of different material. By placing weights in the suspended box (the slide being loaded) force was applied in a direction *parallel* to the sliding surfaces, and when the slide began to move the weight of the small box was a measure of the frictional resistance.

In a particular experiment, the weight of the body on the slide being one ton, a force of 350 lbs. was required to cause it to move.

$$\frac{350}{2240} = 0{\cdot}156 = \mu_1$$

which is called the coefficient of friction, while

$$350 \text{ lbs.} = \text{R}$$

is known as the total force.

The coefficient of friction may be defined as that value which, when multiplied by the pressure normal to the surfaces in contact, gives the measure of the maximum frictional resistance to motion.

Making W the weight normal to the surfaces :—

$$\frac{\text{Frictional resistance}}{\text{Normal weight}} = \frac{\text{R}}{\text{W}} = \mu_1 = \text{Coefficient of friction.}$$

Static and Kinetic Coefficients.—In some cases it has been found that the force R required to keep a body in motion differs from that required to move it from a state of rest. Obviously there must be two coefficients of friction of which the static (μ) may differ from the kinetic (μ_1). As a rule the kinetic coefficient, or coefficient of friction of motion, is alone of importance in machine work, for owing to the freedom or elasticity of the moving parts, or the vibrations generated at starting, the static coefficient does not make itself seriously felt. Hence the term "coefficient of friction" means "coefficient of kinetic friction," unless otherwise stated.

The excess of the static coefficient over the kinetic is most marked in the case of substances such as timber, whose surfaces may be sensibly indented by pressure. When such surfaces have remained for some time in contact under pressure, and at rest relatively to each other, considerable force steadily applied is required to cause them to slide. A similar effect in the resistance to motion is shewn in the process of starting a heavy goods train. With all the couplings tight, and the train at rest, the engine is unable to set the wagons in motion. The driver, therefore, reverses his engine until a sufficient proportion of the buffers are in contact and the couplings slack; he is then enabled to set the wagons in motion one at a time, and so deal with the static or low-speed friction in detail.

Solid Friction.—*Condition of Contact Surfaces.*—The friction between solid surfaces depends so largely upon their nature and condition that, even between similar materials, the friction coefficient is a very variable quantity. However, certain relations have been found to exist between it, the load, the contact area, and the velocity of rubbing. These relations are generally known as the laws of solid friction. They were partly enunciated by Coulomb about a hundred years ago, as the result of his own investigations and of those of previous workers on the subject of friction.

From what has been said regarding the influences which modify friction, it is clear that we are seldom dealing with the actual contact of metal with metal, for all prepared surfaces speedily become contaminated. They are then covered by an extremely thin film of foreign matter—in other words, they are *partially lubricated.* We have already instanced many cases in which the effects of such conditions can be detected. The following may not, however, be out of place here:—

A smooth file passed over a freshly prepared surface will be found to cut well, even when gently pressed against the metal, but if the hand be passed over the metallic surface the film of grease thereby deposited will so lubricate it that considerably greater pressure on the file is now needed to cause it to cut. If it were not for the presence of this contamination film, soft or tough metals, such as tin, wrought-iron, brass, etc., would at once seize if rubbed together even at low speeds. Even with moderate loads, inequalities of the surfaces may project through the film and largely increase the frictional resistances. Until this takes place, the value of the friction-coefficient seems to depend as much upon the smoothness of the surfaces and the nature of the foreign substances interposed as it does upon the nature of the materials in contact.

Rennie's Experiments.—Rennie[*] made a number of experiments on the coefficient of friction between certain metals at moderate speeds.

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[*] *Phil. Trans. Roy. Soc.*, 1829, p. 143.

From the smallness of the coefficient of friction with light loads it would appear that he experimented with contaminated surfaces. The following table gives some of the results he obtained:—

TABLE I.—COEFFICIENTS OF FRICTION BETWEEN METAL SURFACES.

	Brass.	Steel.	Cast-iron.	Wrought-iron.	Tin.
Brass,	**·175**	·139	·141	·135	...
Steel,	·139	**·146**	·151	·189	...
Cast-iron,	·141	·151	**·163**	·170	·179
Wrought-iron,	·135	·181	·170	**·160**	·181
Tin,	...	...	·179	·181	**·265**

Brass upon other metals gives the least frictional resistance, and tin upon other metals the highest average resistance. Tin upon tin and brass upon brass both give high figures—they are evidently, even under small loads, shewing signs of incipient seizing, owing to the rupture of the interposed film at numerous points. These coefficients are, however, much greater than those given by certain antifriction alloys when working upon iron or steel. Prof. R. H. Smith, who has submitted the alloy known as 'magnolia metal' to a variety of tests, gives the following figures, the bearing running dry:—

Nominal pressure lbs. per sq. in.	Speed in feet per min.	Coefficient of Friction μ_1.
99·5	52·3	·0713
99·5	62·7	·0663
99·5	78·4	·0618

Owing to the low friction-coefficient of this metal, a bearing may be run at considerable speed without serious injury resulting. The metal also answers well for bearings which have to carry heavy loads and run at moderate speeds, or which, owing to their positions, can only be supplied with water.

Friction and Speed.—In all cases the static coefficient is sensibly the same as the low-speed kinetic coefficient with imperfectly lubricated metallic surfaces, such as might be used for bearings; but between oak and oak and other soft materials, the kinetic friction at the speeds used in practice is considerably less than the static friction. Jenkin and Ewing * found, however, that the change in the value of the friction-coefficient is not abrupt. In fact, it is highly probable that in the cases where the static coefficient differs from the kinetic, the latter gradually changes when the velocity becomes extremely small, so as to pass without discontinuity into the former.

From a number of experiments made by Prof. Kimball † it would also appear that, although there is no abrupt transition between the static and kinetic coefficients, the friction of motion is not always less than the friction of rest. This is more particularly the case when the loads are small or the surfaces are lubricated.

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* *Proc. Roy. Soc.*, 1878, p. 509.

† *American Journal of Science*, 1877, p. 353.

With clean or nearly clean surfaces, and light loads, Prof. Kimball found that the kinetic coefficient of friction at very slow speeds was greater than the static coefficient, but that with increasing speed the coefficient reached a maximum and then decreased. This he illustrated by an experiment which measured the friction of a leather belt hung over a cast-iron pulley. To one end of the belt a known tension was applied by means of a fixed weight; to the other end a spring dynamometer was attached. The tension of the ends of the belt being known, the coefficient of friction was easily found. In the following table the coefficients given are relative only:—

TABLE II.—RELATIVE COEFFICIENTS.

Feet per Minute.	Relative Coefficients.
18	·82
92	·93
660	1·00
1190	96
1980	·82
2969	·69

Prof. Kimball considers that the results he obtained reconcile the apparently conflicting statements of Morin, Bochin, Hirn, Coulomb, and others, for these investigators experimented under very different conditions of velocity, pressure, etc.

Morin experimented under conditions which gave him a coefficient approaching the maximum, and thus his results were approximately constant for all the speeds tried. Bochin experimented with railway trains; his conditions were high speeds, hard contact surfaces, and great intensity of pressure. These circumstances, under some conditions of lubrication, favour a coefficient *decreasing* as the velocity increases. Hirn, on the other hand, employed very light pressures, less than two pounds on the square inch, and kept his contact surfaces so thoroughly lubricated that the friction was rather between oil and oil than between two metallic surfaces. These conditions, at ordinary speeds, favour a coefficient *increasing* as the velocity increases.

Theory of Solid Friction.—Prof. Hele Shaw * has attempted to account for the laws of solid friction in the following manner. Supposing the surfaces to be smooth and worn to their normal condition, there are even then only a certain very limited number of points in contact, and further wear merely removes groups of particles, leaving other hollows, or, if no wear is taking place, merely displaces the projecting particles. Any increase of pressure brings a larger number of particles into contact, and so increases, to a proportional extent, the friction, or amount of rubbing and consequent heat produced. Hence the friction varies with the pressure. For low velocities, the constant resistance simply depends on the number of particles in contact, and, as this at any point is the same, the friction is not altered; when, however, the velocity is very high, it may be that the surfaces are slightly separated, and the friction is thereby reduced; and it may also be that prominences on one surface periodically displaced, but not permanently removed, may not regain their position with sufficient rapidity to make contact with as many particles on the other surface as they otherwise would.

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* *Cantor Lectures on Friction*, 1886, p. 13.

Laws of Solid Friction.—The laws of solid friction as enunciated by Coulomb are approximately correct for moderate speeds and ordinary loads, but, as they are not applicable at all speeds and loads, the laws of friction between clean or slightly contaminated surfaces may be more correctly stated as follows:—

1. The frictional resistance is approximately proportional to the load on the rubbing surfaces.

2. The frictional resistance is slightly greater for large areas and small pressures than for small areas and great pressures.

3. The frictional resistance, except at very low speeds, decreases as the velocity increases.

The truth of the first law is easily demonstrated by a machine such as Morin's.

With a slider of cast-iron on a slide of the same metal:—

A weight of	56	lbs. requires	8	lbs. to draw it along.
„	28	„	4	„
„	14	„	2	„

For the coefficient of friction of cast-iron upon cast-iron we have, therefore,

$$\frac{8}{56} = \frac{4}{28} = \frac{2}{14} = \cdot 143 = \mu_1.$$

Rennie obtained ·163 for this coefficient. The value of μ_1 is, therefore, according to these figures, approximately independent of the area of the surfaces and the load, provided abrasion does not take place, but it varies with the condition of such surfaces.

Effects of Speed.—For the effects of speed to be ascertained, either the metals in contact must be such that they will not seize as they become heated, or one or both of the contact surfaces must be continually changing. Both these conditions are fulfilled by railway brakes. When the wheel is revolving and rubbing against the brake block the contamination of both surfaces is practically rubbed away, and the metals come into close contact. Dissimilar metals are, therefore, used—generally cast-iron blocks on steel or wrought-iron tires. The clean tire as it revolves is stationary with regard to the rails, and the coefficient there is practically the static. In the following table will be found the results obtained by Galton and Westinghouse * for cast-iron blocks upon steel tires. The coefficient decreases greatly as the speed increases, and also as the blocks become heated after prolonged contact.

TABLE III.—FRICTION OF BRAKES.

Average Speed.	Coefficient of Friction between Cast-iron Brake-blocks and Steel Tires.		
Miles per hour.	1st 3 seconds.	5 to 7 seconds.	12 to 16 seconds.
0	·408 calcd.	·285 calcd.	·237 calcd.
5	·360 exptl.	...	...
10	·320 „	·209 exptl.	...
20	·205 „	·175 „	·128 exptl.
30	·184 „	·111 „	·098 „
40	·134 „	·100 „	·080 „
50	·100 „	·070 „	·056 „
60	·062 „	·054 „	·048 „

The next table gives the coefficients for steel tires upon steel rails.

TABLE IV.—FRICTION OF WHEEL ON RAIL.

Average Speed.	Coefficient of Friction between Steel Wheel Tires and Steel Rails.
Miles per hour.	From commencement of Experiment to end of 3 Seconds.
0	·141 calculated.
10	·110 experimental.
15	·087 „
25	·080 „
35	·051 „
45	·047 „
50	·040 „

Between the brake-block and tire the friction is high, for there is no foreign substance on the surfaces. In the case of the wheel upon the rail the case is different; here the tire is slipping over a more or less contaminated surface and the frictional resistance is smaller. The adhesion of wheels to rails yields a very variable coefficient of friction, ranging roughly from 0·3 to 0·1, according to the state of the weather. Taking the coefficient of the rolling friction of the wheel upon the

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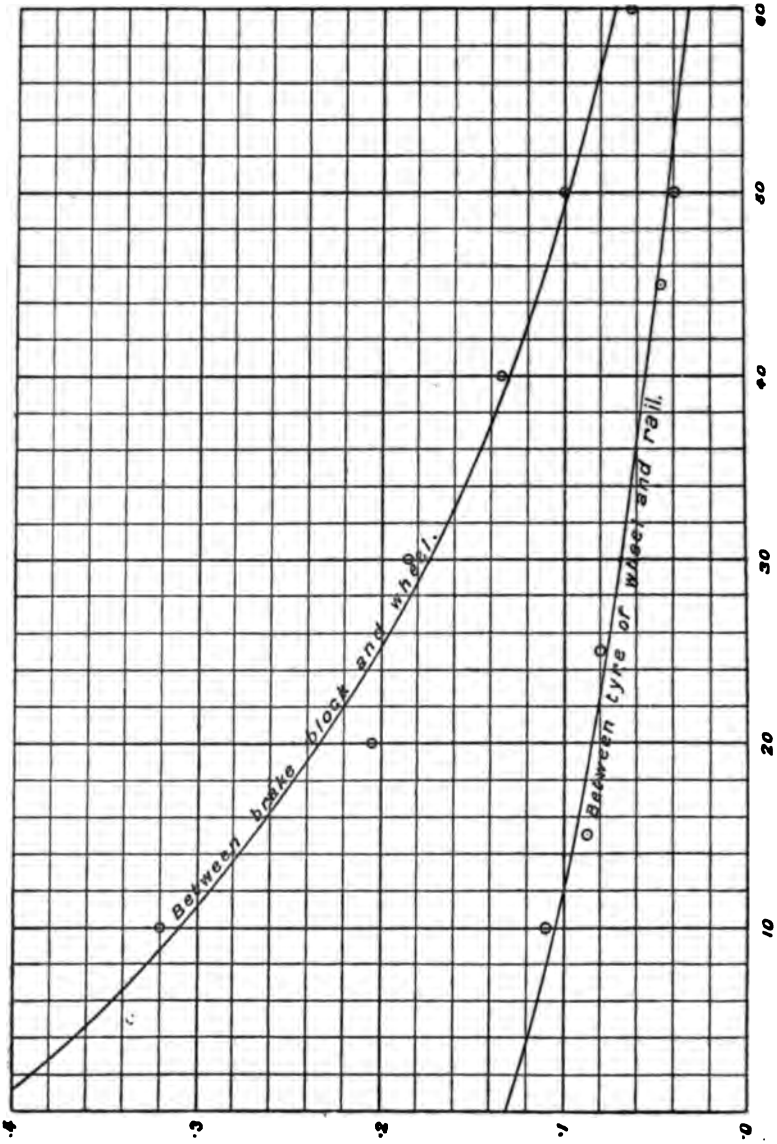
* *Engineering*, London, Aug. 23, 1878.



Coefficients of Friction. FIG. 1.

rail to be 0·2 at all speeds, in ordinary weather at 25 miles per hour we may make the weight upon the blocks equal to the weight of the vehicle, but at higher speeds, say 60 miles per hour, about two and a half times this pressure will, at the moment of application, barely skid the wheels.

On the diagram (fig. 1) some of the figures obtained by Galton and Westinghouse have been plotted with the corresponding theoretical static coefficients. The curves drawn through them are logarithmic curves, the rate at which the friction decreases being approximately proportional to the coefficient of friction at each speed. In other words, the slope of the curve at any point is proportional to the length of the corresponding ordinate, and if the logs. of the ordinates had been plotted the result would have been straight lines.

This decrease of the friction with increasing speed occurs both with the friction between the wheel and rail and with that between the brake-block and tire. In the former instance, the contact surface of the tire is constantly passing over fresh rail, which maintains unaltered the nature of the contamination and keeps the temperature from unduly rising; but between the tire and the brake-block there is no such constant supply of foreign material, and the contact surfaces consequently abrade each other and heat very rapidly. This heating would seem in a great measure to be the cause of the decrease of the friction when the surfaces have been in contact several seconds.

Rolling Friction.—When a roller passes over an elastic surface the contact is not line contact; both the roller and the surface upon which it rests are, according to Osborne Reynolds,* deformed by the pressure.

In fig. 2 an iron roller is represented moving over a surface of rubber. The rubber is distorted by the weight of the roller, and slides or rubs against it at points near C and D. For some distance on each side of the centre, P, there is no slipping, and this area of no slip increases with the friction between the surfaces. When both the roller and the surface upon which it rests are distorted the conditions are similar.

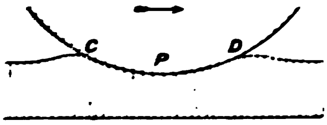


FIG. 2.

It is conceivable that the use of an unguent for ball or roller bearings may so increase the area over which slipping takes place that the resistance to rolling may be actually increased. The lubricant, however, in some measure, prevents the wear of the surfaces. In the case of rubber tires, rolling over rough, uneven ground, such slipping is not large, and the resistance to rolling is correspondingly small.

The laws of rolling friction would appear to be identical with those of sliding friction with the *proviso* that the resistance varies inversely as the radius of the rolling body. The law may be expressed as follows:—

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* *Phil. Trans. Roy. Soc.* 1876 p. 155.

$$R = \mu_1 \frac{W}{r} \quad . \quad . \quad . \quad . \qquad (2)$$

where μ_1 = the coefficient of friction, W = the load on the roller, r = the radius of the rolling body, and R = the frictional resistance.

The rate of slipping at the contact surfaces is so slow that the coefficient of friction, although it probably decreases as the speed increases, does so very slowly.

Cause of Heating.—The energy which is expended in overcoming the frictional resistance of two rubbing surfaces and in keeping them in motion is converted into heat, and raises the temperature of the masses in contact above that of surrounding objects. When the amount of friction is small the rise of temperature is also small, but should the frictional resistance become large from any cause, the heating of the materials in contact may become so great that the opposing surfaces either become brittle, melt, or even weld together. It is clear that some relationship exists between the work done and the heat produced. The significance of this relationship was first grasped by our countryman, James Prescott Joule, who experimentally demonstrated that a given amount of work, however expended, always produces a fixed quantity of heat. In such cases as the lifting of a weight or the bending of a spring, energy is rendered potential, but this stored energy can likewise produce its proper equivalent of heat.

Before the relationship between work, energy, and heat can be formulated accurately, we must be able to measure both work and heat in some exact manner. The unit of heat used in this country is the quantity which will raise one pound of water, at its maximum density, one degree F. in temperature. When the C.G.S. or metric system is used it is the quantity of heat which will raise one gramme of water from 4° C. to 5° C. Work, on the other hand, is measured by the product of the average resistance and displacement. Thus, in the case of a sliding surface, if the force required to maintain the surfaces in relative motion be one pound, and the distance travelled be 779* feet in each second of time, then the work done each second is 779 foot-pounds. This amount of work has been proved to be just sufficient to raise one pound of water, when at its maximum density, one degree in temperature. 779 foot-pounds is called the mechanical equivalent of heat, and the constancy of its value under all conditions has established on a firm basis the law of the conservation of energy. To the engineer this is one of the most important generalizations ever arrived at, as it affords a ready means of answering many problems which would otherwise be difficult to solve.

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* *Science Progress*, vol. i. p. 127.

Making W = the total pressure in lbs. on the rubbing surface:—

μ_1 = coefficient of friction.

v = speed of rubbing surface in feet per minute.

Then the frictional resistance $= W\mu_1$.

The foot-pounds of work done per min. $= W\mu_1 v$.

And the thermal units generated per min. $= \frac{W\mu_1 v}{779}$.

We thus see that the heat liberated by any bearing surface is proportional to the friction. In some mechanical oil-testing machines the rise of temperature which occurs is measured and is taken as an indication of the resistance to motion the surfaces offer. The actual rise of temperature depends, of course, not only upon the rate at which heat is liberated, but also upon the conductivity of the heated surfaces. The frictional resistance cannot, therefore, be proportional to the rise of temperature.

CHAPTER II.

LIQUID FRICTION, OR VISCOSITY, AND PLASTIC FRICTION.

Introductory.—Before mineral oils were introduced as lubricants, engineers had little reason to study the theory of viscosity or to specify the particular fluidity of the oils they wished to make use of, for the number of animal and vegetable oils available for lubrication is limited, and the degree of viscosity they exhibit does not vary much in different samples, a little experience being usually sufficient to determine the most suitable description of oil for the purpose in view. But since the introduction of mineral lubricating oils, which can be prepared of any desired viscosity, the measurement of this property and the study of its influence upon lubrication have assumed great practical importance.

In this chapter we purpose discussing the nature of viscosity and viscous flow, including the theory of the viscometer. The bearing of viscosity on lubrication will be discussed in Chapter IV. on "The Theory of Lubrication"; and practical viscometry, or the method of measuring the viscosity of lubricating oils, will be reserved for Chapter VI. on "Physical Methods of Testing Lubricants."

Nature of Viscosity.—All liquids exhibit viscosity, although in varying degree. Thus, if a vessel of water be tilted and then quickly brought back to its original position, so as to set the water in oscillatory motion, it will be found that with each swing the amplitude of the oscillation becomes smaller, and that in a very short time the movement dies away or becomes imperceptible, and the surface of the liquid comes to rest in an exactly horizontal position.

If a similar experiment be made with sperm oil, a much greater resistance to movement will be observed; the oscillations produced will not only be much slower, but will also be fewer in number. Very viscous oils, such as castor, and viscid liquids like glycerine and treacle, will not even oscillate; such liquids merely flow steadily until their free surfaces are again horizontal. In all cases the movement ceases sooner or later, and it is the internal friction or viscosity of the liquid which arrests the motion.

Cohesion and Viscosity.—Some writers have assumed a relationship between viscosity and cohesion, but no connection has yet been proved to exist. Considerations such as the following will shew that there is no necessary relation between them.

A sphere of soft iron may be slowly rotated around the pole of a powerful magnet with very little difficulty, although considerable force is required to draw the ball and magnet apart. Similarly, the molecules of water move about each other with great freedom, and the liquid has a very low viscosity in consequence; yet, according to the calculations of Young and Dupré, the force required to tear the molecules apart is equal to a pressure of about 25,000 atmospheres.

Viscous Flow and Lubrication.—As the value of an oil for lubricating purposes depends very largely upon its viscosity, the laws of viscous flow will be considered at some length. We will endeavour to state the mathematics of the subject in as simple a manner as possible, illustrating by means of diagrams those conditions of flow a fairly complete explanation of which is necessary in order to obtain a proper understanding of the part viscosity plays in lubrication.

The conditions of motion of a fluid film inclosed between two relatively moving surfaces differ somewhat from the flow of the same liquid through a capillary tube. In the one instance we have the conditions obtaining between lubricated surfaces, and in the other the conditions of flow under which viscosity is most readily and accurately measured.

Viscous Flow between Parallel Horizontal Planes having Differential Tangential Motion. — When a fluid lubricant is interposed between two solid surfaces, one of which is in tangential motion and the other at rest, that portion of the fluid which is in contact with and adherent to the moving surface is constrained to move with it, while that portion which is adherent to the surface which is at rest remains motionless. Between the two surfaces the fluid may be regarded as consisting of a series of superposed layers, each moving at a speed proportional to its distance from the solid fixed surface. This, the simplest form of viscous flow, is illustrated in fig. 3.

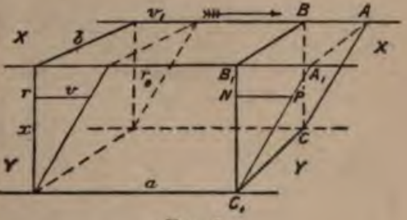


FIG. 3.

A stratum of a viscous medium is inclosed between two parallel planes, XX and YY, the upper of which is supposed to be moving with uniform velocity in the direction of the arrow, whilst the lower remains fixed. The motion of the fluid must be considered as having reached a steady state, the force producing the motion being supposed to act solely along the plane XX in the direction of the arrow.

The liquid medium may be regarded as made up of a series of infinitely thin superposed planes (a coarse illustration being a pack of cards), the topmost and lowest of which are held by cohesion in immediate contact with the solid surfaces. The topmost plane of liquid is, therefore, carried along by the moving surface XX, and the lowest plane is held stationary by the fixed surface YY. The intermediate planes of the liquid derive their motion solely from that of the plane XX, the force acting upon which is propagated downwards from stratum to stratum by the internal friction or viscosity of the fluid. As the frictional resistance is absolutely uniform throughout the fluid, each liquid plane must move over the one immediately below it exactly the same distance in the same time; and, therefore, any row of points in contiguous planes, forming at one moment the vertical straight line C_1B_1, will have moved, after a certain interval, into positions on the inclined straight line A_1C_1. If the length of the line A_1B_1 be taken to represent the velocity with which the upper plane is moving, then the length of the line PN will represent the velocity of the fluid at any point in the plane passing through N. In such a case, which is virtually that presented by a properly lubricated bearing, there is no friction between the two solid surfaces, for they do not touch, and yet force, continuously applied, is required to keep the surfaces in relative motion. The frictional resistance, as already pointed out, is wholly due to the sliding of the liquid layers, one over the other, *i.e.*, to the resistance offered by the liquid to shear. It has been necessary to deal with this subject in some detail, for the action of a lubricant is sometimes stated to result from the *rolling* of the molecules of the lubricant over each other, and over the solid surfaces between which they pass. Such a view, however, cannot be justified by an appeal to experiment.

The force required to maintain continuous relative motion between opposing plane surfaces, such motion being of the nature of a shearing stress, is measured by the stress per unit area of either of the planes. Thus we may write

$$F = fA \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where F is the total force, f the force per unit area, and A the area of the planes over which the stress acts.

Since no stresses other than those transmitted by shear act on the mass of liquid abr_0, any section through it parallel to the two bounding planes is exposed to the same stress per unit of area as is the liquid in contact with the planes. If A_1C_1 becomes the position after the lapse of one second of a normal line of section, such as B_1C_1, then the inclination of the line A_1PC_1 will be the same throughout its length, and it must be a straight line. Also the length B_1A_1 represents the velocity of the upper plane, and the length NP the velocity at a distance B_1N from XX.

Hence, since $\frac{NP}{NC_1} = \frac{B_1A_1}{B_1C_1}$ we may write $\frac{v}{x} = \frac{v_1}{r_0}$, where v is the velocity at a distance x from YY, and v_1, and r_0 are their values at the surface XX.

The stress f is, therefore, proportional to $\frac{v}{x}$, which we may call the rate of distortion, and we may make

$$f=\eta\frac{v}{x} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where η is a constant which varies with the temperature for any liquid, and is known as the coefficient of viscosity of that liquid.

Further,

$$F=fA=fab \quad . \; . \; (3); \qquad =\eta\frac{v}{x}A \quad . \; . \; (4); \qquad =\eta\frac{v_1}{r_0}A \quad . \; . \; (5)$$

$$\therefore \quad \eta=\frac{Fr_0}{v_1A} \quad . \; . \; (6); \qquad \text{and } v_1=\frac{Fr_0}{\eta ab} \quad . \; . \; (7)$$

Also the rate of distortion . . . . . $=\frac{v_1}{r_0} \quad =\frac{F}{\eta A}$ . . . . . (8)

If v_1, A, and r_0, are each made unity, then $\eta=F$, and the viscosity η is measured by the tangential force per unit area of either of two horizontal planes at the unit of distance apart, one of which is fixed, while the other moves with unit velocity, the space between the planes being filled with the viscous substance.

By the establishment of the above simple working definitions we are able to form equations applicable in all problems involving viscous flow.

Both in the measurement of the viscosity of various liquids, and in the problems which have to be solved in the theory of lubrication, it is necessary that we should be able to find the volume of the liquid displaced under varying conditions. Although this can be simply accomplished by methods involving the calculus, it is better for the clearer understanding of lubrication problems to attack the matter geometrically.

The volume V swept through by any cross section $B_1B\ C_1C$ in moving to the position $A_1A\ C_1C=\frac{v_1br_0}{2}$ . . . . (9)

and this is a measure of the volume of liquid displaced.

Substituting for v_1 its value from equation (7)

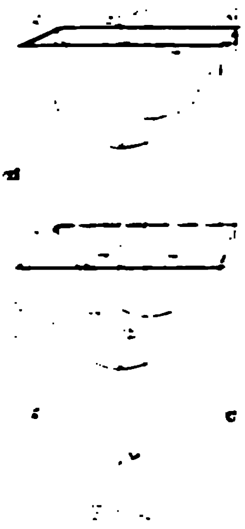
$$V=\frac{Fr_0^2}{2a\eta} \qquad . \quad . \quad . \quad . \quad . \qquad (10)$$

and for F its value from (3)

$$V=\frac{fr_0^2b}{2\eta} \qquad . \quad . \quad . \quad . \quad . \qquad (11)$$

Viscous Flow under the Action of Gravity between Fixed Planes.—We have hitherto considered only the conditions of flow which result from a stress applied solely at a liquid surface parallel to the direction of flow, the viscosity of the fluid setting in motion the whole mass in such a way that the rate of shear is everywhere the same. But when the liquid flows between two fixed plane surfaces, parallel to each other, and the force setting the fluid in motion acts either upon each particle of the liquid, or equally over the whole of a section normal to the direction of flow, the velocity at different points in the liquid is not proportional to the distance from the solid surface, $\frac{v}{x}$ ceases to equal $\frac{v}{r_0}$, and the rate of shear is not the same at all points.

[illegible] measurement of the viscous constants of [illegible] conditions [illegible] when lubricants are [illegible] conditions of flow which obtain [illegible] which it is advisable to [illegible] over the gap between the conditions under which a lubricant really works and those under which its viscosity is measured.



[illegible] the rate of shear, which is the [illegible] is indicated by the slope of the [illegible] but when the [illegible] of shear varies regularly across the [illegible] becomes curved, as is shewn [illegible]. When the viscous liquid is supposed to be flowing between two vertical parallel plane surfaces [illegible] and [illegible] under the influence of uniform pressure acting on the surfaces [illegible] on each side of [illegible]. Here, in place of a force [illegible] acting on unit area of [illegible] parallel to the direction of motion, we have a pressure [illegible] acting on unit area of the surface [illegible] normal to the direction of flow. This force may result either from the pressure of a liquid column, or it may be regarded as the effect of gravity acting with an equal force on each particle of the liquid. In either case the nature of the flow is the same, but it is more convenient to treat it as being due to a pressure [illegible] acting on a surface normal to the direction of flow.

[illegible] then the whole pressure [illegible] total pressure on half [illegible]

[illegible] the rate of shear at the boundary

$$= [illegible] \qquad (12)$$

We also find that at any distance r from YY the rate of shear $=\frac{pr}{\eta x}$. (13)

and we see that the rate of shear is directly proportional to the distance *r* from the plane *YY*. That is to say, at any point C (fig. 5) in the liquid the rate of shear is proportional to BC. Now $\frac{AB}{BC}$ is the rate of shear, CA being tangential to the curve at C. Draw CD perpendicular to CA to cut the centre line in D. Then we have $\frac{BD}{BC}=\frac{BC}{BA}$. But $\frac{BC}{BA}$ is proportional to $\frac{1}{CB}$ (see above). Therefore $\frac{BD}{BC}$ is proportional to $\frac{1}{BC}$, or BD is constant.

ut BD is the subnormal of the curve $C_1E_1C_1$, which can easily be shewn e a parabola, and therefore the volume of fluid passed on each side of , in unit time, is half the volume of a parabolic prism $C_1E_1C_1$ of length b. ow, since the curve is a parabola $B_1E_1 = \frac{1}{3}B_1A_1$,

$\frac{B_1A_1}{B_1C_1} = \frac{pr_0}{\eta a}$ (equation 12) $B_1A_1 = \frac{pr_0^2}{\eta a}$

$$B_1E_1 = \tfrac{1}{2}B_1A_1 = \frac{pr_0^2}{2\eta a} \quad . \quad . \quad . \quad . \quad (14)$$

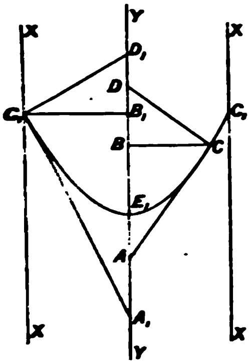


FIG. 5.

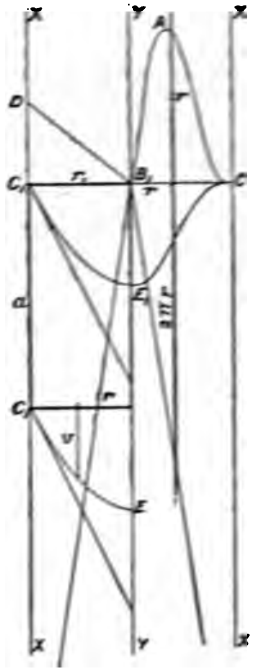


FIG. 6.

Now, the volume enclosed by the parabolic curve $C_1E_1 = \frac{2}{3}$ area of the base × the perpendicular height.

Therefore the volume passed in unit of time on each side of the plane

$$Y = \tfrac{2}{3} \times r_0 b \times \frac{pr_0^2}{2\eta a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$= \frac{pr_0^3 b}{3\eta a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

nd the volume passed in any given time (t) will be

$$\frac{pr_0^3 bt}{3\eta a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Viscous Flow through Capillary Tubes.—As will be seen when the theory of lubrication comes to be discussed the conditions of viscous flow obtaining between plane surfaces are all important. Still such conditions are not those under which the coefficient of viscosity η is most accurately and easily measured. The most concordant values have been obtained by measuring the rate of flow through capillary tubes in which, as between plane surfaces where the flow results from the pressure of a given head of liquid, the rate of shear is greatest at the bounding surface.

Fig. 6 shews diagrammatically the conditions of flow obtaining in a capillary tube, at a point some distance from the end at which the liquid enters, the flow having reached a state of equilibrium; for at the inlet end the effects of inertia manifest themselves.

In a portion of tube of length a, the whole pressure on the cross section C_1C_1 tends to shear the liquid at the bounding surface, and the area over which this pressure acts is equal to $2\pi r_0 a$. Now, the area of the cross section of the tube $=\pi r_0^2$. Therefore, the total pressure over the cross section $=p\pi r_0^2$, and from (8) the rate of shear at the boundary $=\dfrac{p\times\pi r_0^2}{\eta\times 2\pi r_0\times a}$

which resolves itself into $\dfrac{pr_0}{2\eta a}$ . . . . (18)

In the case of a small cylinder of liquid concentric with the tube and of radius r, the rate of shear at its boundary $=\dfrac{pr}{2\eta a}$ . . . . . . (19)

Therefore, the rate of shear is directly proportional to the distance from the centre line of the tube, and the curve indicating the rate of distortion is, as in the case of the parallel planes, a parabola; and the volume passed in unit of time is the volume of a paraboloid of revolution, having a base of radius r_0 and a height $=B_1E_1=\frac{1}{2}B_1A_1$ (fig. 5).

From equation (12) we have

$$\frac{B_1A_1}{B_1C_1}=\frac{pr_0}{2\eta a} \qquad (20)$$

Therefore
$$B_1A_1=\frac{pr_0^2}{2\eta a} \qquad (21)$$

and
$$B_1E_1=\tfrac{1}{2}B_1A_1=\frac{pr_0^2}{4\eta a} \qquad (22)$$

Now the volume of a paraboloid of revolution $=\frac{1}{2}$ the area of the base $\times$ the perpendicular height. Therefore, the volume passed in unit time

$$=\tfrac{1}{2}\times\pi r_0^2\times\frac{pr_0^2}{4\eta a} \qquad (23)$$

or
$$\frac{\pi}{8}\cdot\frac{pr_0^4}{\eta a} \qquad (24)$$

And the volume V passed in any given time $=\dfrac{\pi}{8}\cdot\dfrac{pr_0^4t}{\eta a}$ . . . . (25)

We may find an expression for the viscosity of the liquid from the above, by substituting for p its equivalent in terms of the head and density of liquid, and the force of gravity, *i.e.*,

$$\eta = \frac{\pi g \rho h r_0^4 t}{8 V a} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Poiseuille was the first to demonstrate experimentally that the volume of liquid passed by a capillary tube is directly proportional to the pressure urging it along, and to the fourth power of the radius of the tube, and inversely as its length. On this account the above is known as *Poiseuille's formula*, and may be used, after making a small correction for h, for the purpose of calculating *absolute* viscosities.

Physical and Mechanical Viscosity.—As Osborne Reynolds has pointed out,[*] it by no means follows that for each particular liquid a fixed value of η need necessarily exist, such that f calculated by equation (2) agrees with the values of f determined by experiment for all values of v and r_0. As a matter of fact experiment shews that liquids have apparently two viscosities; for, as is well known to engineers, in large pipes the resistance to flow varies as the square of the velocity, and not directly as the velocity. When such is the case η is not constant in value.

Carefully conducted experiments by Coulomb, Poiseuille, and others, on the rate of flow through long capillary tubes, have proved conclusively that the resistance under certain conditions is proportional to the velocity, and that η has then a constant value. Poiseuille's experiments also proved that the volume passed varies as the fourth power of the radius of the tube. Such being the case we may safely regard the flow of liquids through tubes of very small bore as being controlled by the physical viscosity of the liquid, and use equation 26 as a means of calculating the value of η when the other values have been determined experimentally. But the fact must not be lost sight of, that to obtain a correct result, the size of the tube, the intensity of the pressure producing the flow, and the viscosity of the liquid must bear certain relations to each other. The reasons for this have been successfully worked out by Prof. Osborne Reynolds, who demonstrated that the two viscosities, physical and mechanical, result from a change in the character of the flow from that of direct parallel to that of sinuous or eddying motion.

To shew this change in the nature of the flow when the velocity reaches a certain value, a long, bell-mouthed glass tube was immersed horizontally in a tank of water. One end of the tube passed through the side of the tank and was bent vertically downwards for several feet, being terminated by a stop-cock. By partially opening or closing this cock the water could be made to flow through the tube at any desired speed. Terminating opposite the bell-mouthed tube, and immersed in the water, was fixed a much smaller tube through which a highly coloured stream of water was discharged. When the speed of flow was small, the coloured stream passed through the whole length of the bell-mouthed tube as a perfectly straight line (fig. 7). When, however, by opening the cock, the speed reached a certain value, the band of colour suddenly broke up and discoloured the

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[*] "Theory of Lubrication," *Phil. Trans. Roy. Soc.*, 1886, p. 165.

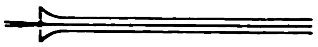

Fig. 7.

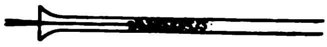

Fig. 8.

whole of the liquid. By the intermittent light of an electric spark, the mass of colour resolved itself into a series of more or less distinct curls shewing eddies, as in fig. 8.

A series of experiments made it clear that so long as the flow remained direct and steady, the resistance varied directly as the velocity, but as soon as the critical speed was reached the resistance became proportional to the square of the speed, or thereabouts, and sinuous motion was set up. The critical speed was found to vary directly as the viscosity and inversely as the diameter of the tube and the density of the liquid.

Although it is an experimentally ascertained fact that there is a certain critical speed for each size of tube and each liquid below which the resistance varies directly as the velocity, and above which the resistance is proportional to the square of the velocity, the reason for the change in the nature of the flow has yet to be satisfactorily explained.

We have thus two essentially distinct viscosities: the one a mechanical viscosity, arising from the irregular motion of the fluid, and the other a true physical property of the fluid depending in some way upon its structural peculiarities. Although the value of the physical viscosity determines in some measure which of the viscosities shall control the flow of the fluid, when the flow is once in accordance with the mechanical viscosity the physical viscosity does not in any direct way shew itself. Thus, when in a particular tube the velocity of oil or treacle is sufficient for the resistance to vary as the square of the velocity (*i.e.*, for the liquid to flow with sinuous motion) the resistance is practically the same as it would be with water at the same velocity, although the physical viscosity of water may be more than a hundred times less than that of the oil.*

The critical velocity is rarely if ever reached by lubricating films, and when the lubrication is perfect, the resistance to relative motion is due to the physical viscosity of the lubricant.

The possibility of slipping at the boundaries, or of internal disruption, must not be lost sight of. So far, no indication of this has been perceived, either in water or liquid lubricants, even when the tangential stresses to which they have been subjected in narrow channels have been as high as 0·702 lb. per square inch.

Determinations of viscosity made by measuring the resistance offered to the motion of discs or cylinders immersed in liquids are, for the most part, unsatisfactory. In such cases turbulent motion is locally, if not generally, set up, and the results are misleading. For this reason such methods of measuring, or attempting to measure, the viscosity need not be referred to, as they are not of any practical value, except for exceedingly viscous liquids.

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* Osborne Reynolds, *Phil. Trans. Roy. Soc.*, p. 153, 1895.

Effects of Temperature and Pressure.—With rise of temperature the viscosity of liquids decreases—sometimes very rapidly. In this respect liquid lubricants differ greatly from each other. Oils of animal and vegetable origin retain their viscosities better than those of mineral origin, but they all become very mobile with rise of temperature, and lose, in a great measure, their lubricating value. Not only is it necessary, therefore, to keep a liquid whilst testing it at a very uniform temperature, but the effect of varying temperature must be carefully noticed.

Viscosity varies also with pressure, water having its viscosity decreased by this means. On the other hand, concentrated solutions of common salt have their viscosities increased by pressure, as has also oil of turpentine. No experiments, however, seem to have been made to ascertain the changes of viscosity which lubricating oils undergo when under great and varying pressures. Such information would be valuable, since lubricating films are frequently subjected to very considerable loads.

Conditions determining Steady Flow.—The formulæ obtained for the flow of liquids through capillary tubes only hold good, as we have seen, so long as the flow is direct and not sinuous. When high pressures and comparatively short tubes of large bore are employed, the liquid, if not very viscous, ceases to flow steadily in paths parallel with the bounding walls; the motion becomes sinuous, and the resistance offered to the flow of the liquid ceases to be directly proportional to the velocity. The length and diameter of the capillary tube, and the pressure with which a liquid (of given viscosity and density) is forced through it, must therefore be properly proportioned to each other, or the physical viscosity cannot be even approximately determined.

Osborne Reynolds* has found that for the flow to be steady the product of the mean velocity v, the radius of the tube r_0, and the density of the liquid ρ, divided by the viscosity η, must—in the case of a round tube—be less than a certain constant c.

$$\frac{r_0\bar{v}\rho}{\eta} < 700 \quad . \quad . \quad . \quad . \quad . \quad (27)$$

This constant (700) is the same whatever system of weights and measures is adopted, for the divisor and dividend each involve the same powers of length, mass, and time.

When the value of c is less than 700, the volume of liquid passed is, as already demonstrated, $\frac{\pi}{8} \cdot \frac{h\rho g r_0^4 t}{\eta a}$

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* *Phil. Trans. Roy. Soc.*, 1895, p. 149.

and the mean speed of flow

$$\bar{v} = \frac{V}{\pi r_0^2 t} = \frac{\pi}{8} \cdot \frac{h\rho g r_0^4 t}{\eta a \pi r_0^2 t}$$

$$= \frac{h\rho g r_0^2}{8\eta a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Substituting in equation (27) the value of $\bar{v}$ in equation (28) we have

$$\frac{r_0^3 h\rho^2 g}{8\eta^2 a} < 700 \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and

$$\frac{hgr_0^3}{a} < 5600\frac{\eta^2}{\rho^2} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Unless the proportions of the viscometer, and the physical properties of the liquids used in it, be in accordance with the requirements of this equation, the flow will be unsteady, and the true viscosity cannot be calculated. When absolute viscosities are desired, the viscometer should be designed so as to make the value of c as small as possible.

But sinuous motion, even when c is very much greater than 700, does not set in, as will be seen from fig. 8, immediately the fluid enters the pipe. With tubes having trumpet-shaped orifices the disturbances appear and the flow becomes sinuous at about thirty diameters from the end; but when the end is flat the disturbances approach the inlet end more closely. The flow of liquids in very short tubes is, therefore, free from eddies, even though the viscosity of the liquid, the diameter of the tube, and the rate of flow may be such as to make c greater than 700. In such cases, although the flow is steady throughout the tube for some distance from the inlet, the velocities are not such that the rate of distortion is proportional to the distance from the centre. Such short tubes may, therefore, be used to obtain comparative, but not absolute viscosities, even with very mobile liquids. The conditions which determine whether the flow shall be steady or unsteady are often very complex, for the stream lines may be parallel, as in pipes or between parallel surfaces; convergent, as in a conical mouthpiece; or, when the motion is reversed, divergent.

The circumstances which conduce to a direct steady motion are—(*a*) high viscosity or fluid friction; (*b*) a free surface, as in a fountain jet; (*c*) solid converging boundaries; and (*d*) curvature with the velocity greatest outside.*

The circumstances which conduce to sinuous motion are—(*a*) particular variation of velocity across a stream, as when a stream flows through still water; (*b*) solid bounding walls; (*c*) solid diverging boundaries; and (*d*) curvature with the velocity greatest inside.

Energy of Flow through Capillary Tubes.—When the coefficient of viscosity is calculated from Poiseuille's formula (26), it is assumed that the character of the motion is the same at all sections of the tube, and that all the energy supplied to the liquid is converted into heat within the tube. But the coefficient so obtained is only approximately correct, for not only is there some resistance to the flow of the liquid outside the tube, but the steady condition of flow within the tube is not reached until the liquid has travelled some distance from the orifice. The liquid, when it approaches the critical speed, often possesses considerable velocity, and an appreciable amount of energy then exists as kinetic energy in the issuing fluid. As this energy results from the pressure due to the head of liquid, a deduction on this account should be made if accuracy is aimed at.

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* *Proc. Royal Institution*, 28th March 1884.

We have, consequently, four sources of error to consider, and if possible allow for—(*a*) external viscous resistance in the liquid at the ends of the tube; (*b*) abnormal conditions of flow at inlet end of tube; (*c*) surface tension effects at discharge orifice; and (*d*) energy of flow at point of discharge. No corrections have yet been devised for *a* and *b*. They are small and become practically negligible when the tube is long; but when the tubes, compared with their diameters, are so short that sinuous motion is not set up, even when the value of c is much greater than 700, the necessary correction often becomes so large that the true viscosity cannot be calculated even approximately. Neither can an allowance for *d* be made, for a state of equilibrium is not reached even at the end of the tube, and the energy of flow cannot be found.

The third source of error (*c*), however, is of some importance, and is sometimes met by so designing the viscometer that the discharge end of the capillary tube is always immersed in the liquid. An allowance on this head is difficult to make when the liquid flows directly into the air from the orifice, for its value depends upon the curvature of the liquid surface as well as upon the actual tension of the surface, *i.e.*, upon the dimensions of the drops, or upon the form of the liquid stream and the surface tension of the liquid.

The fourth (*d*) is important, and can be accurately estimated when the tube is long and a steady condition of flow is set up, for there is no reason to suppose that any change takes place in the distribution of energy as the discharge orifice is approached.

Correction for Energy of Flow.—That a correction for the energy of flow is necessary was pointed out by Hagenbach,* and his method of measuring it has been very generally followed. Lately, however, Wilberforce † has demonstrated that the correction suggested by Hagenbach is too small, and that the true correction is furnished by deducting from the mean head, h, a quantity$=\frac{\bar{v}^2}{g}$, where $\bar{v}$ is the mean velocity of flow through the tube. A geometrical method of demonstrating this is shewn in fig. 6, in which the ordinates of the parabolic curve C_1E_1 give the velocities of flow at any distance from the centre line. If they are regarded as representing the successive values of $\frac{v}{v_1}$, where v_1 is the maximum velocity, then B_1E_1 is equal to unity on this scale.

The curve CE_1 is plotted on the same scale to represent the corresponding values of $\left(\frac{v}{v_1}\right)^3$; and finally the ordinates of the curve B_1AC are made proportional to $\left(\frac{v}{v_1}\right)^3 2\pi r$. The ordinates of B_1D are equal on the same scale to $\left(\frac{\bar{v}}{v_1}\right)^3 2\pi r$.

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* *Pogg. Ann.*, cix., 1860.

† *Phil. Mag.*, May 1891.

Now, if we consider a thin cylinder of liquid of radius r, length a, and thickness τ, its energy is

$$\frac{2\pi r a \tau v^2}{2g}$$

and is, therefore, proportional to the area of the part of the curve B_1AC included between the corresponding ordinates.

Hence the total area of the curve B_1A_1C is proportional to the energy of flow, and in the same way it can be shewn that B_1C_1D would be proportional to the energy of flow if the velocity were constant across the section. If the areas B_1AC, B_1DC_1 be now measured up with a planimeter, B_1AC will be found to be equal to just twice B_1DC_1. Hence, the true energy of flow is equal to twice that obtained on the assumption that the velocity is uniform all over the section.

In this latter case the correction would evidently be $-\frac{\bar{v}^2}{2g}$. Hence, the true correction is $-\frac{\bar{v}^2}{g}$, as shown by Wilberforce and others.

When all the values required for calculating the viscosity by Poiseuille's formula (26) are known, the deduction necessary in the value of h is easily obtained, for

$$\bar{v} = \frac{V}{t\pi r_0^2} \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Substituting this value for $\bar{v}$ we obtain

$$-\frac{V^2}{g\pi^2 r_0^4 t^2} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

as an expression for the required correction.

Viscometer Proportions.—In order to obtain the value of η with accuracy it is necessary that the correction for energy shall be small—say one or two per cent. A formula for calculating this percentage is obtained as follows:

The energy correction being equal to $\frac{\bar{v}^2}{g}$

$$h : \frac{\bar{v}^2}{g} :: 100 : \%.$$

Therefore
$$\frac{100\bar{v}^2}{hg} = \%.$$

Substituting for $\bar{v}^2$ the value from (28)

$$\frac{100 g^2 \rho^2 h^2 r_0^4}{64\eta^2 l^2 hg} = \frac{100 g\rho^2 h r_0^4}{64\eta^2 l^2} = 1{\cdot}563\frac{g\rho^2 h r_0^4}{\eta^2 l^2} = \%.$$

Inlet End Resistance.—This disturbing factor has not yet received anything like complete experimental treatment.

Fig. 9 shews the inlet end of a capillary tube into which a liquid is flowing. The speed of flow everywhere decreases as we leave the centre line, and increases as the orifice is approached. The liquid is consequently undergoing shear both inside the tube and outside near its ends, and the resulting resistance must be added to that in the tube if we are to obtain the true viscosity. This resistance, and that due to the abnormal conditions of flow just inside the tube, we may allow for by somewhat increasing the length of a. Some experiments, the results of which we shall give when we come to deal with practical viscometry, and which were made for the purpose of calibrating viscometers having short capillary tubes, shew that when the rate of flow is so slow that the energy correction is negligible, the viscosity, calculated by Poiseuille's formula, is somewhat greater than experiment with very long tubes proves it to be. The value we obtain for water at 20° C., using a viscometer with a long and narrow bore, is about 2 per cent. greater than that obtained by Thorpe and Rodger.[*]

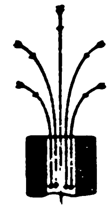

FIG. 9.

Plastic Friction.—Plastic substances, such as tallow, lard, moist china-clay, etc., differ from viscous fluids inasmuch as they require that the shearing stress shall reach a certain value before continuous shear takes place. They can, therefore, permanently retain their shapes when the stresses are unequal in different directions; *i.e.*, they can transmit stresses without undergoing continuous shear. Sometimes the plastic yield point is very low, and the substance behaves much as does a viscous liquid. A layer of lard, for example, placed between two smooth surfaces, which are prevented thereby from touching, requires the exercise of a definite stress to cause tangential motion; but when once relative motion is set up by the action of a sufficiently powerful force, the resistance increases with each increase in the rate of shear. In the case of plastic friction, therefore, we have something corresponding to the static friction of solid surfaces in contact; but whether the plastic yield-point varies with the pressure normal to the direction of flow (shear), or whether the resistance is proportional to the rate of shear is uncertain.

The distinction between plastic or soft solids and viscous ones was clearly recognized by Maxwell.[†] He says, "when continuous alteration of form is only produced by stresses exceeding a certain value, the substance is called a soft solid, however soft it may be." "Thus, a tallow candle is much softer than a stick of sealing-wax; but if the candle and the stick of sealing-wax are laid horizontally between two supports in summer, the sealing-wax will, in a few weeks, bend with its own weight, while the candle remains straight. The candle is, therefore, a soft solid, and the sealing-wax a very viscous fluid."

It is evident that the same substance, for instance, lard or tallow, may act when in use either as a plastic lubricant or a viscous one, for at moderately high temperatures these substances melt, and may become viscous lubricants, *i.e.*, true oils.

At first sight it would seem that the resistance to shear offered by a plastic substance would be so great that it would be altogether unsuitable for lubricating purposes. But such is by no means the case; indeed, at very low speeds the resistance to motion of a film of plastic grease is often smaller than that of an oil film, for the grease film is much thicker, and the rate of distortion is less.

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[*] *Phil. Trans. Roy. Soc.*

[†] *Theory of Heat*, p. 303, 1894 (1894 Edition).

When two surfaces are forced together, between which there is a plastic substance, the pressure or stress is transmitted from point to point, shear takes place, and the intervening lubricant is expelled. A viscous liquid under such conditions is expelled until the bearing surfaces come into contact, or the surface forces prevent further escape; such, however, is not the case if the intervening lubricant be plastic, for the nearer the surfaces approach the less the shearing stresses become, and long before the surfaces can touch they reach the plastic yield point, and further flow ceases.

In fig. 10 are shewn the experimentally ascertained curves of shear for plastic clay. Here the surfaces AB and CD are approaching without tangential motion. The curves shewing the conditions of distortion will be seen to differ remarkably from those of a viscous fluid, which take the form of parabolas (fig. 28).

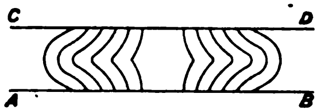

FIG. 10.

Unfortunately there is very little experimental data to guide us here, except such as is furnished by the actual working of vehicles lubricated by greases. This aspect of the question can be more satisfactorily dealt with when we come to deal with the theory of lubrication, for, as we have pointed out, the actual resistance to motion offered by oil and grease films depends upon their thickness, area, and the temperature produced by the friction, as well as upon the absolute viscosity or plasticity.

Many of the greases used for lubricating purposes are mixtures of soft solids and viscous oils or soaps. On standing, the oils sometimes separate out from the solids as minute globules, suspended in a solid matrix. When kneaded, however, the oil is spread out and forms continuous films, which much reduce the resistance to shear.

CHAPTER III.

SUPERFICIAL TENSION.

Lubrication and Superficial Tension. — *Lubricating Films.* — Although Prof. Osborne Reynolds* has proved that the results obtained by Mr. Beauchamp Tower† with lubricated journals were due to the viscous nature of the liquids employed, it has been clearly recognised by engineers that when the supply of oil is insufficient, the rate of friction very slow, or the load excessive, lubrication depends upon other less generally understood and somewhat obscure properties. As a matter of fact a liquid may have the required viscosity and yet not be a lubricant. J. Veitch Wilson states that *body* or viscosity is not the only property by which the antifrictional value of an oil is determined. The differentiating principle must, he urges, be attributed to some other property. Thurston states that a liquid, to act as a lubricant, must possess "enough 'body' or *combined capillarity and viscosity* to keep the surfaces between which it is interposed from coming in contact. . . ." Although he does not substantiate this statement in detail, there is every reason for regarding it as true, if not taken too literally.

To be lubricants, liquids and soft solids should feel oily or greasy. As capillarity, oiliness, greasiness, wetting, emulsification, etc., are either wholly or in part phenomena resulting from superficial tension, this property will be dealt with at some length, so far as it seems to throw light upon lubrication problems; for the phenomena resulting from superficial tension are among the most interesting and important that can engage the attention of either the chemist or the engineer, and they manifest themselves in a great variety of ways. Unfortunately, the values of many of the physical constants, a knowledge of which is required—such as the thickness of various liquid films when spread over or between solid surfaces—have not in many cases been measured.

Soap (Bubble) Films.—If the looped end of a piece of wire be dipped into a solution of soap and water, on its removal there will be seen stretched across the loop, a thin diaphragm of liquid. Such a film possesses considerable elasticity and strength, as may be proved by placing upon it a small moistened wire ring, which it supports without breaking. In other words, the film resembles a sheet of indiarubber, some force being required to stretch or distort it. Prof. Vernon Boys[*] has described a number of very beautiful experiments, illustrating the tension properties of such liquid films. He used for this purpose a mixture of 1 part, by weight, of sodium oleate dissolved in 40 parts of distilled water. When solution was complete, one-third of its volume of glycerine was added to the liquid and the whole was allowed to settle. The liquid was then siphoned off from the impurities which had risen to the surface and was clarified by the addition of a few drops of ammonia. Films made of this mixture last a very long time, and very instructive studies of superficial tension phenomena may be made by their means. Such films consist of two surface layers which have closed together by the withdrawal of the water from between them, and each layer is under the same degree of stress. The surfaces of all liquids exhibit allied phenomena.

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* *Phil. Trans. Roy. Soc.*, 1886, p. 157.

† *Proc. Inst. Mech. Eng.*, 1884.

Wetting of Solid Surfaces.—A slip of *clean* glass dipped into a vessel of water, and then withdrawn, will be found to have a thin film of water adhering to it. The film so formed consists of two surface layers, one in contact with the air, and the other in contact with the glass. In this case the mass of glass plays the same part as the air in a bubble. If the plate be held vertically and partially immersed in a vessel of clean water, the external surface layer of the film on the glass becomes continuous with the surface layer of the water, and it will be observed that the water surface, where it meets the solid, is distorted, as shewn in fig. 11.

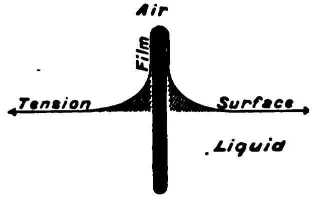

Fig. 11.

Here we have the surface layer of the liquid in the vessel in a state of tension, and also the external surface layer on the raised glass plate in a similar state of tension, and the two stresses are acting at right angles to each other. To balance these tensions a small quantity of water, shaded in the figure, is lifted above the general level, and the free surface becomes curved. The weight of the water or other liquid raised is proportional to the superficial tension of the vertical surface layer, which covers the glass and is in contact with the air, just as the load on a spring-balance is proportional to the stress on the spring.

The superficial tensions of different liquid surfaces vary very considerably, that of mercury being greater than that of water, whilst the superficial tension of the latter is greater than that of oils.

Theory of Superficial Tension.—*Molecular Attractions.*—Some reasons have already been adduced in support of the view, that the molecules of solids powerfully attract each other when brought into close juxtaposition. This is equally true of the molecules of liquids, which, in spite of their fluidity, require the expenditure of a considerable amount of energy to separate their molecules completely. At sensible distances, the attractive forces between molecules are inappreciable, but when the distances separating them become infinitesimal the forces become extremely powerful. It has been computed that such attractions become perceptible when the distances separating the molecules are reduced to $\frac{50}{1,000,000}$ millimetre.

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[*] *Phil. Mag.*, May 1888, p. 409.

Berthelot found that water could sustain a tension of about 50 atmospheres, applied directly, and the phenomenon of retarded ebullition, described by Dufour, helps to confirm this view. In a vessel containing a mixture of linseed oil and oil of cloves, the latter observer immersed drops of water, which were still seen to be swimming about after the temperature had been raised to 356° F. The pressure of aqueous vapour is, at this temperature, nearly ten atmospheres, or about 147 lbs. per square inch. Hence the cohesion of the water must be able to support a tension of at least 132 lbs. per square inch. In these experiments the water was carefully freed from dissolved air, etc.

Intensity of Molecular Stresses.—Evaporation or boiling may be regarded as a process in which the cohesive forces of the molecules of the liquid have been completely overcome, the heat rendered latent being a measure of these forces. This view Lord Rayleigh [*] regards as substantially sound, and he calculates that, on this hypothesis, the cohesive force of water is 25,000 atmospheres.

Lord Kelvin has pointed out [†] that the experimentally ascertained attractive forces are millions of times greater than would follow from the law of gravitation, on the supposition that matter is perfectly homogeneous; but as we know that matter is not perfectly homogeneous, by postulating sufficient heterogeneity, the attractive forces *may* be accounted for without assuming any attractive force other than that in accordance with Newton's law.

It is admitted that, as there is every reason to believe that the atoms and molecules never come into actual contact, this attractive force, which is operative over a limited range, must be balanced by a repulsive force of suitable intensity, operative over a different range; consequently, the molecules approach each other until their attractive and repulsive forces are in equilibrium.

Condition of Surface Molecules.—It is clear that the molecules in the interior of a liquid are all in the same condition of stress. On the other hand, the molecules at or very near the surface are differently situated, for the attractive forces are then by no means equal in all directions. In other words, the molecules at or very near the surface have their attractive forces only partially satisfied, and the unbalanced stresses are constantly tending to reduce their number and, therefore, to decrease the surface area. Any increase of the surface area involves an increase in the number of molecules whose attractions are not satisfied, and to effect this, force must be exerted. We thus have all liquid surfaces tending with considerable force to contract their areas, and exhibiting the phenomenon of superficial tension. The resultant effect of the mutual attractions between different portions of a fluid really gives the same result as would be obtained if the liquid were[*] "absolutely deprived of the attractive forces of its molecules, and its whole surface were coated over with an infinitely contractile film, possessing a uniform contractile force." This is a convenient way of explaining the fact that a mass of liquid, left entirely to the action of cohesive forces, assumes a spherical figure, but it is important not to lose sight of the idea that the spherical form is the result of an endeavour of the particles to get as near to each other as possible.

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[*] Rayleigh, *Phil. Mag.*, Dec. 1890, p. 286.

[†] *Popular Lectures and Addresses*, vol. i. p. 59.

Liquid Interfaces.—But even when we have the surfaces of two different liquids in contact, the molecular stresses may not be completely satisfied, for the ranges and intensities of the attractive and repulsive forces of the two kinds of molecules may be very different. There, consequently, remain unbalanced forces, and the interface is in a condition of strain.

Lord Kelvin, who carried out a number of experiments on the behaviour of dissimilar liquids when in contact, found it convenient to employ bisulphide of carbon, and a solution of sulphate of zinc, as no immediate chemical or physical action results on bringing such liquids together. Additional advantages arose from the fact that bisulphide of carbon assumes an intense violet coloration with iodine, which enabled observations to be more readily noted; while the sulphate of zinc solution could be adjusted to any required density. When both liquids were at the same density, it was found that globules of either suspended within the other assumed a spherical condition as the result of the tension developed at their surfaces of contact.

Miscibility of Liquids.—At present our knowledge of the conditions which determine whether two given liquids will diffuse into each other, or remain apart, is very limited; indeed, a knowledge of their comparative surface tensions affords us little or no help in this direction. Two drops of mercury, for instance, have the same surface tensions. The tension, however, of the junction surface between two drops of mercury is zero, and they unite to form one drop. Many liquids, on the other hand, which have very different surface tensions, will also diffuse into each other and mix in all proportions.

Marangoni states that in all cases in which liquids do not mix, that possessing the smallest surface tension will spread over the one which has the greatest. At one time water and mercury were supposed to be exceptions, but it has been shewn that water will readily spread over a mercury surface if the latter be free from surface contamination. This subject has lately engaged the attention of Lord Rayleigh,[†] who concludes that the interfacial tension between any two bodies is proportional to the square of the difference of certain values, peculiar to them, analogous to density in the theory of gravitation.

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[*] Kelvin, *Popular Lectures and Addresses*, vol. i., 1891, p. 16.

[†] "Theory of Surface Forces," *Phil. Mag.*, p. 463.

Thus, suppose we have three fluids, the interfaces of which meet along a line perpendicular to the paper (see fig. 12). Making T_1, T_2, and T_3 the interfacial tensions, and denoting the property analogous to density by σ_1, σ_2, and σ_3, then, according to Lord Rayleigh,

$$T_1 \propto (\sigma_3 - \sigma_1)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$T_2 \propto (\sigma_2 - \sigma_1)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$T_3 \propto (\sigma_3 - \sigma_2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It will be found that whatever the three respective values of σ in the above expressions, the interfacial tension T_1 between the liquids of greatest and least 'density' will always exceed the combined tensions T_2 and T_3 of the other interfaces, and that consequently the liquid of intermediate tension will always be drawn in between those of greatest and least surface tension.

This theory has an important bearing upon diffusion phenomena, for when two miscible liquids are brought into contact the interface immediately disappears, and there is substituted for it a thick layer, across which the value σ changes gradually from that of one liquid to that of the other. According to this the whole surface tension force of any two miscible liquids in contact may be considered as distributed over the space in which diffusion is taking place, and, as the number of contiguous layers may be regarded as infinite, the force between each layer becomes infinitely small, and it has been shewn that their sum must be zero.

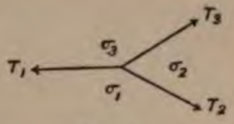

FIG. 12.

Surface Tension of Solids.—It was not until the surface tension phenomena of solids were recognized that the theory assumed its present form, for it will at once be seen that the above applies to the surface molecules of solids as well as liquids, and also to the molecules at the bounding surfaces of solids and liquids, even when in contact with gases.

In solids, as in liquids, the molecules attract each other powerfully, and the surface molecules are in the peculiar condition of having the stresses arranged differently in directions parallel to and normal to the surfaces. The surfaces of solids must, therefore, be in a state of tension; but in their case the stresses are not sufficiently powerful to produce perceptible deformation of the mass. Very viscous liquids, such as pitch, do shew the reality of the stress, even when the liquids are so viscous that they act very much as solids do; for in the course of time they round off their sharp corners and shew all the peculiar surface tension phenomena of mobile liquids. A piece of glass, having sharp cutting edges, when heated rounds off its corners. It would scarcely be logical to argue that superficial tension only comes into existence the moment the solid is softened by the heat. Rather must we consider that the surface was in a condition of stress before the glass was heated, but that the tension only shewed itself when the mass ceased to be rigid.

Contact of Liquids and Solids.—Although it might be thought that we should be unable to experimentally demonstrate the existence of surface tension in solids, the behaviour of liquids and gases in contact with solids is really in accordance with theory. A particular liquid does not, for instance, act towards all solids in the same way. Water will wet and spread over a clean sheet of glass, but when a drop of water is placed upon a sheet of solid paraffin wax it draws itself up into a bead. Mercury will not wet any known solid with which it does not amalgamate. From this we conclude that mercury has a greater surface tension than glass, and that water has a surface tension greater than that of paraffin wax, but less than that of glass. All lubricants have surface tensions much smaller than those of the metallic surfaces to which they are applied: they consequently spread over them and wet them.

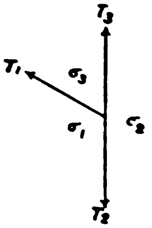

FIG. 13.

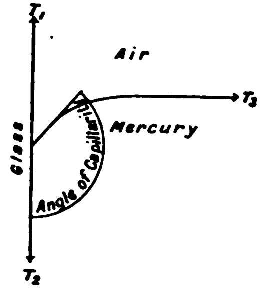

FIG. 14.

Although, according to Marangoni and Laplace, three fluids cannot rest in contact, yet if two liquids and a solid be brought together, the latter being a body of intermediate surface tension, neither of the liquids can spread completely over the solid, for the tension at the interface between the solid and any one of the liquids can never exceed that at the other two.

Fig. 13 illustrates this. Here the solid σ_2 has a flat surface and against it rest the liquids σ_1 and σ_3, the former having a smaller and the latter a greater tension than that of the solid. So long as the magnitudes of the surface tensions are thus distributed then T_1 (the interfacial tension between the liquids of greatest and least 'density') is greater than the sum of T_2 and T_3, and the point of meeting is drawn along the surface of the solid until T_1 assumes such an angle with the solid surface that the forces are in equilibrium. It will be noticed that the tension T_3 is tending to wrinkle the solid surface and draw it between the two liquids, so as to arrange the three bodies in the order of their surface tensions.

When a liquid of high surface tension, such as mercury, is resting upon a solid of lower surface tension, such as glass, although the liquid does not spread over the solid and *wet* it, there is really a close union of the two masses, which can only be parted by the exercise of force or the interposition of a liquid of intermediate surface tension. Indeed, so close is the contact of mercury and glass that the vacuum in a barometer remains unaffected for years.

Fig. 14 illustrates the conditions obtaining in a tube immersed in mercury. Here T_2 is so much more powerful than T_1 that the mercury surface is depressed until T_3 makes such an angle with the surface of the solid that T_1 and T_3 together balance T_2.

When oils and water are brought into contact with metals the liquid of least surface tension is not necessarily easily displaced by the liquid having the greatest surface tension, for everything depends upon which liquid touches the metal first. Thus, if the metal be made perfectly clean, and then dipped into oil, water cannot penetrate between the solid and the lubricant, for the metallic surface has become so contaminated by the oil that it behaves as though it were a solid surface of smaller surface tension than water. On the other hand, if the clean metal be dipped into water first, then the water is not displaced by the oil, and we have the liquids in the order of their surface tensions. This reasoning accords well with what is known concerning the action of water in steam cylinders, for when copious condensation takes place, and the water cannot get away freely, efficient lubrication is almost an impossibility. This, of course, does not apply to cloudy steam impinging upon rubbing surfaces. In such a case each minute drop of water may be covered by a pellicle of the lubricant which necessarily reaches the metallic surface first and lubricates it.

The readiness, however, with which solid surfaces become contaminated by many substances, and the difficulty experienced in cleaning them again, is satisfactorily explained by assuming that the surface molecules exert a very considerable attractive force on surrounding matter. Indeed freshly formed solid surfaces at once attach to themselves from the air an exceedingly thin coating of moisture, which is in a few hours replaced or supplemented by a layer of grease. Such contamination films are probably not always continuous sheets covering the surfaces and separated by an abrupt line of demarcation from the solid, but mixtures of liquid or gaseous molecules with the surface molecules of the solid.

Although Lord Rayleigh's theory concerning the comparative intensities of the surface tensions of liquids and solids serves to explain very clearly some of the most striking surface tension phenomena, it must not, as he says, be followed too far; for there still remain numerous phenomena which it fails to explain, or is even in apparent conflict with. However, even if the hypothesis is too narrow to accord with all the facts, it illustrates clearly the main points with which we have to deal.

Lubricating Films.—*Oiliness.*—When a glass surface is rubbed y a wet finger, care having been taken to remove all grease, the riction between the skin and the glass is very considerable. If the urface be the edge of a wine glass, the alternate seizing and freeing f the contact surfaces causes the glass to vibrate and produce a musical ote. Even such a thick liquid as glycerine, when the rubbing movement is slow, fails to keep the surfaces apart and prevent the glass from feeling harsh. A little grease, fat, or good lubricating oil will, on the other hand, remain as a fairly thick film between the surfaces, and enable them to slip freely over each other even at low speeds.

We may, therefore, take it that a film of pure water between two solid surfaces is so thin that it fails entirely to keep their asperities from interlocking; whereas lubricating oils form films on such surfaces which succeed, more or less, in preventing the asperities from interlocking, and so greatly reduce the friction between them.

In many respects the property which some liquid films possess of powerfully resisting all attempts to reduce their thicknesses below certain fixed values, and even, as we shall see, of preventing bubbles from bursting, is a most valuable one. It is evidently in no direct way dependent on viscosity, for many very viscous liquids fail entirely to form lubricating films. Nor is it measured by the superficial tension of the liquid. All we have a right to say is that when the superficial tension of the lubricant is less than that of the solid, the liquid spreads itself over the surface of the latter, and when it has so covered the surface, its lubricating value depends upon the thickness of the layer it forms, and the extent to which it resists efforts made to expel or extrude it.

Stability of Liquid Films.—Very little is known concerning the thickness or viscous properties of liquid films, other than can be gathered from friction phenomena. For example, the experiments of Prof. Thurston * on the static friction of surfaces lubricated with lard oil and sperm oil would seem to prove that although the former is nearly twice as viscous as the latter, the lard oil gives the smallest coefficient of friction, and therefore must form the thickest lubricating film.

A difference has also been noticed in the relative stability of bubbles blown from different liquids. Pure water, for example, will not form permanent bubbles—the film rapidly gets thin in places and bursts, owing to the superior tension of the surrounding parts. On the other hand, when soap is added to the water the film refuses to be reduced to a thickness of less than twelve millionths of a millimetre, for with decreasing thickness its strength increases. This minimum thickness of a soap film is sufficient to prevent polished surfaces separated by it from touching each other except at a few points and, therefore, constitutes it a lubricant.

Profs. Reinold and Rucker † have studied the properties of soap films with great care. When first formed, the surfaces enclose a considerable volume of liquid which does not in any way affect the tension of the surface layer, and when this portion of the liquid has drained away, the film remains at a constant thickness of about twelve millionths of a millimetre. At this figure the surfaces may be considered to have closed together and the films look black all over, for they reflect very little light and have ceased to shew Newton's rings. The stability and uniform thickness of these thin films indicate that, when a certain minimum thickness has been reached, the tensile strength increases and prevents rupture.

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* *Friction and Lost Work*, Third Edition, p. 316.

† *Phil. Trans.*, 1883, p. 645, and 1886, p. 627.

The majority even of very viscous mineral oils are deficient in oiliness, for they do not form sufficiently thick films to keep the static friction as low as can be obtained by using animal or vegetable lubricants. This has led to the manufacture of 'compound' and 'thickened' oils. The former are mixtures of mineral with animal and vegetable oils. The 'thickened' oils contain various ingredients, such as soaps, which are supposed to act by increasing the viscosity, but which may have the same effect upon mineral oils as on water, *i.e.*, they may cause them to form thick lubricating films instead of thin ones.

Experiment only can determine whether the latter mixtures are really useful; the substances added are not always adulterants, but rather ingredients added for the purpose of conferring upon the lubricants properties in which they are deficient.

Circumstances which Modify Surface Tension.—*Temperature.*—If a thin film of oil be spread over the upper surface of a metal plate, and a hot iron be caused to touch the underside, the oil will shrink away from the heated spot and leave it almost clean. This is caused by a decrease in the tension of the heated oil surface and the consequent drawing away of the oil by the cooler surrounding film.

It appears that the surface films of all liquids diminish with rise of temperature, and less energy is required to separate their molecules. Thus, in converting water into steam at 212° F., 965·7 units of heat per lb. are required, whereas at 374° F. 649·0 suffice.

Owing to this reduction of surface tension by heat, the oil film on a heated bearing is drawn away from the rubbing surfaces by the greater superficial tension of the film on the surrounding cool parts, and the lubrication becomes more and more defective as the bearing gets hotter, owing to the creeping away of the oil and its lessened viscosity.

Solubility.—We have hitherto spoken as though the contact surfaces of dissimilar liquids, gases, and solids were really sharp surfaces of demarcation between the opposing molecules of the media in contact. Such, however, is not really the case, for many liquids are *partially*, if not wholly, soluble in each other. Ether, for instance, dissolves in water, but when more than one part of ether is added to ten parts of water the excess of ether remains separate from and insoluble in the aqueous liquid. Similarly, ether dissolves about three per cent. of water. The interfacial surface between mixtures of these liquids does not, therefore, separate ether from water, but rather abruptly separates mixtures of the two liquids from each other.

Superficial Solubility.—There is reason to believe that the solubility of liquids, and also of gases in liquids, follows different laws in surface films, where the molecules are in peculiar conditions of strain, than it does in the interior of liquids.

This may be shewn in many ways. For instance, a thin disc of camphor so placed that it is half immersed in a clean water surface, in the course of a few hours, is cut through by the superior solvent action of the surface film. In some cases the action is reversed, and the mass of the liquid displays a greater solvent power than the surface layer.

The superior solvent power of a water film over the mass of the liquid has been shewn by Lord Kelvin and Dupré, who found that, at the first moment of their formation, surfaces of soapy water have hardly less tension than pure water, but that the molecules of the dissolved soap gradually collect in the film and greatly modify its properties.

This concentration of the dissolved substance in the surface film also takes place when the interface is one separating a solid from a liquid, for it has been long known that vinegar can be separated from water by the immersion of very fine sand in the mixture. Potato spirit, if filtered through clean sand, passes water first, then alcohol, and finally alcohol plus fusel oil.

Dr. Gore* made a number of interesting experiments on the behaviour of various aqueous solutions in contact with finely divided silica. He found that, on agitating solutions of acids, alkalies, and salts with this powder, and allowing it to subside, the solid in many cases abstracted as much as 80 % of the dissolved compound.

This concentration of a dissolved substance on the contact surface of the liquid with the solid, enables a lubricant to be applied with ease, and without serious waste, to the friction surfaces of hydraulic machinery. The more or less soluble lubricant is added to the water before it enters the pipes, and then by concentrating upon the surfaces lubricates them and greatly reduces the friction and wear.

Contamination of Liquid Surfaces.—Lord Rayleigh and Agnes Pockles† have shewn the remarkable effects that even traces of foreign substances exert upon the surface tension of water. It is in some measure this marked action of traces of impurity which makes experimental work on surface tension phenomena so difficult, and which places such obstacles in the way of the practical application of our present knowledge. Agnes Pockles used a rectangular trough 70 cm. long, 5 cm. wide, and 2 cm. deep, filled with water to the brim. A strip of tin about 1½ cm. wide was laid across it at right angles to its length, so that the underside of the strip was in contact with the surface of the water and divided it into two portions. By moving this partition, the surface area could be varied to any desired degree. The surface tension was measured by the force necessary to separate a small disc from the surface. A perfectly clean surface was obtained by placing the tin partition at one end of the trough and drawing it across the surface, thereby sweeping off the contamination. Such a surface retains an approximately uniform contractile force, however much the partition may be moved and the area varied. On the other hand, a *strongly* contaminated surface was found to have a variable surface tension.

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* *Chem. News*, vol. lxix. p. 22.

† *Nature*, vol. xliv. (1891) p. 437.

The effects of contamination films may be shewn by sprinkling upon a *clean* surface of water lycopodium grains or other suitable powder. Such a surface, if touched by a needle which has been dipped in oil, will at once become contaminated, and the effect produced by the spreading of the oil over the surface is as though a hole had been pricked in the film, for the dust-covered surface draws rapidly away from the oiled centre and crowds the dust particles towards the edge of the vessel. A drop of spirit allowed to closely approach or touch the water surface weakens the tension of the film in a similar manner.

To shew how greatly the tension of a clean water surface differs from an oiled one, a light rubber ring may be floated upon a clean water surface. The tensions of the surface film being the same inside and outside, the ring, by its elasticity, assumes a circular form. On bringing a little oil into contact with that portion of the water surface outside the ring it loses a comparatively large proportion of its strength. The superior tension of the internal film then distorts the ring or even causes it to collapse completely.

Surface Energy.—*Proportional to Surface Area.*—As any increase in the area of a surface involves the expenditure of work, and as either increase or decrease in the value of the tension of a surface produced by its closing upon another surface, or coming into contact with a contaminating substance, alters the work such a surface is capable of doing, each unit of area of such surface represents so much available energy. Indeed it acts like a stretched sheet of rubber which can do work by contracting. We must, therefore, regard the total energy of a body as not being solely due to its temperature and its volume, but as also depending to a certain extent upon the area of its surface.

The separation of a drop of any liquid into two or more parts can only be accomplished by the expenditure of work, for the volume of a sphere is proportional to the cube of its radius, whereas its superficial area is only proportional to the square of the radius. Thus the finer the state of division of the liquid, the greater the superficial area in proportion to the volume. The total energy of a liquid is therefore increased by breaking it up into separate drops, and the total energy of the mass must include this energy as well as that due to its temperature and volume. A given weight of steam, which is water broken up into separate molecules, has therefore more energy than the same weight of water in its liquid state and at the same temperature.

Emulsions.—Emulsions are generally composed of globules or oily liquids suspended in the form of exceedingly small drops in other liquids in which they neither diffuse nor dissolve. Generally speaking the individual globules may be clearly distinguished under the microscope, as in the case of milk. In some instances each liquid particle is surrounded by a film separating it from the liquid in which it floats.

In other cases when emulsification takes place the liquid forming the matrix has had its surface tension so altered by the introduction of a third substance, or a substance of such a nature, that the film resists rupture and prevents the coalescence of the drops of oil.

Heat of Wetting.—It has been observed that when finely divided silica is moistened with water, or with an aqueous solution of any salt, a rise of temperature results. Here we have a surface between air and silica exchanged for one between the liquid and silica. As water spreads over silica and wets it, the surface tension of silica must be greater than that of water, and that of the interface between these must have some intermediate value. Consequently, when the water wets the silica a liberation of energy takes place and the temperature is increased. Other effects, however, resulting in a liberation of heat, may be produced as well.

It thus seems that the reason why lubricants may be spread over solids and [illegible] the whole of their surfaces is that the liquids have lower superficial tensions than the solids, and the *wet* condition is the one of least potential energy.

A clean glass rod dipped successively into mercury, water, and oil gives very different results. The relative surface tensions of the liquid and solid are not such as to enable the mercury to adhere to the glass permanently. As pointed out previously, the mercury and glass do adhere, but the mercury is drawn off by its weight and strength of film. It is otherwise with water, the smaller superficial tension of which causes it to spread over the glass, which remains wetted when removed from the liquid. When the glass rod is immersed in oil and is then removed, the oil, like the water, remains on the glass, but as a thick instead of a thin film. The reason why a larger volume of oil than of water adheres to the rod is that the viscosity of water is small, whereas the oil is very viscous and flows much more slowly. Sufficient time being allowed, both oil and water run off and leave very thin films on the glass.

Capillarity.—*Capillary Rise in Tubes.*—Although this is merely a striking manifestation of superficial tension, it is commonly known as 'capillary attraction,' having in the first instance been studied in connection with capillary tubes.

When experimenting on capillary phenomena, care should be taken that all the tubes, etc., employed are quite clean. Indeed if the surfaces be chemically clean, and the liquid experimented on possesses a smaller superficial tension than the solid, the liquid will at the moment of contact with the solid rise and wet the whole of its surface. It is, however, better, after cleaning the tube, to moisten it all over with the liquid to be experimented on, and thus ensure that the effects shall not be interfered with by atmospheric impurities.

When a tube which has been cleaned and moistened is dipped into a beaker of water, the liquid rises rapidly in the bore and may reach a height of an inch or more. When this takes place in a moist atmosphere the whole of the surface of the tube, both internally and externally, is covered by a film of water which is continuous with the water in the beaker. On the outside of the tube, the vertical stress of the film raises a small ring-shaped mass of water above the general surface level, the weight of which just balances the tension of the film. On the inside of the tube, the tension of the film covering the walls of the bore draws up a long column of water which also balances the tension of the internal surface film, and is a measure of its pull. Hence the height to which the liquid is drawn up in the tube varies inversely as the radius of its bore.

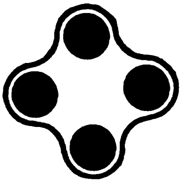

Fig. 15.

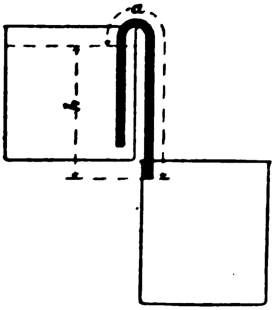

Fig. 16.

But it is by no means essential that, to secure the rise of a liquid column above the general surface, a tube should be used. A few lengths of wire held so as to enclose a small area will also produce the same effect.

Fig. 15 is a section of four parallel wires which dip vertically into the liquid. Between these wires superficial tension surfaces form, and furnish walls which act much as the walls of a rubber tube would, converting the wire cage into a tube up which the liquid rises.

Flow through Wicks.—A worsted string or a lamp wick is really a similar contrivance, and, as the strands are very fine and close together, the liquid often rises several inches. As long as the surface tension of the fluid is less than that of the material of which the wick is made, and therefore wets it all over, the liquid column rises to a height proportional to the surface tension of the fluid. When such a partly immersed wick hangs down outside the vessel containing the iquid, if the lip of the vessel be not too high, then the wick onstitutes practically a number of small siphons, through which the uid flows. In such capillary passages the flow is steady, and the olume passed is directly proportional to the head and inversely proortional to the length of the wick and the viscosity of the fluid.

Fig. 16 shews such a case. Here the height h of the column prolucing the flow is measured from the surface of the vessel to the end f the wick, whilst the length a of the wick gives the length of the apillary passages.

From Poiseuille's formula for the flow of liquids through capillary ubes we find that the volume passed in t seconds is

$$V = C\frac{g\rho ht}{\eta a} \quad . \quad . \quad . \quad . \quad (4)$$

the value of C varies with changes in the size and texture of the wick.

It must be remembered that in the case of siphon wicks the walls of the passages, along which the liquid flows, consist partly of liquid surfaces. Consequently as soon as the suction at the top of the siphon becomes too great, owing to the fall of the surface in the reservoir, for the surface tension to balance it, the liquid walls collapse, air is drawn between the strands and siphoning ceases rather suddenly. On this account the formula (4) does not hold if the long 'leg' of the wick falls so low that the weight of liquid in it shall of itself rupture the external film. Strands of worsted consist of rather coarse fibres and can only be depended upon to raise the liquid over a lip rising about 1¼ inches above the liquid surface. When more powerful lifting action is required, as in lamp wicks and the strands used to supply lubricants to railway axle pads, cotton pleated very finely is used instead of worsted.

All such wicks, pads, strands of worsted, etc., when exposed to the air, absorb moisture and other substances. Oil will not, therefore, flow freely through them until they have been well dried and then wetted with the liquid in which they are to work. The volume of lubricant such wicks will supply depends, as we have seen, not only upon the superficial tension or capillarity of the liquid, but also upon its viscosity. The height to which it rises increases with the superficial tension and the fineness of the external mesh of the wick.

Cohesion Figures.—Although in the practical testing of oils the observation of the curious forms assumed by the spreading of oil drops on clean water surfaces has not yet been found to be of much practical value, cohesion figures are of great interest, and may yet be found of service.

When a drop of oil is allowed to fall on water, although it quickly contaminates the whole of the water surface, the greater portion remains as a lenticular mass, which spreads with greater or less rapidity; becomes perforated with holes and forms beautiful lacelike figures; and finally separates into numerous lenticular discs. Different oils produce in most cases different figures, and these figures are altered by the presence of adulterants. The thickness of the contamination film surrounding the oil discs is exceedingly small — about two millionths of a millimetre—and the tension of this attenuated film would seem to be about as great as that of the combined pull of the oil and air and oil and water surfaces enclosing the lenticular masses of superfluous oil. This tendency of the two surfaces of a film to close together and force the excess of fluid to collect in separate masses resembles closely the phenomena observed in soap bubbles by Profs. Reinold and Rucker, who noticed that the thin black film was often surrounded by one having a thickness 250 times as great.

It is clear, however, that before the significance of the action of the surface forces of liquids and solids upon some of the more obscure phenomena of lubrication can be satisfactorily ascertained, further research upon surface tension phenomena will be required.

Measurement of Surface Tension.—*Tension of Films.*—We have seen that the surfaces separating solid, liquid, and gaseous substances from each other are in a state of tension, and that the magnitude of this tension varies with the nature of the substance or substances in contact; or, when the surfaces are not clean, with the nature and extent of the contamination. Such surfaces act like stretched sheets of indiarubber, but the tension is always the same in all directions, and, when not contaminated, has the same value however much the film may be extended.

In fig. 17 ABCD is a stiff wire frame upon which the cross wire PQ slides freely. In the area enclosed by the wire is a liquid film, a measure of the tension of which is required. This film, it will be remembered, consists of two tension surfaces which pass round and grasp the wire frame and slider on all sides. The two surfaces are separated from each other and from the surface in contact with the wire by an inactive liquid layer of variable thickness. The active liquid surface layer which produces the tension effects has a thickness of about five millionths of a millimetre, the water layer inclosed may be a hundred or more times thicker than this. To prevent the elasticity of the film from drawing the cross wire PQ towards BC, a force F must be maintained acting in the direction of the arrow. If T be the superficial tension and b the distance apart of the wires BA and CD, then, as there are two surfaces to the film, separated by liquid,

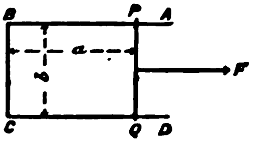

FIG. 17.

$$F=2Tb \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Rise in Capillary Tubes.—The method which has usually been adopted for measuring superficial tension is by ascertaining the height to which liquids rise in capillary tubes. The degree of accuracy obtainable is limited, however, by (*a*) the narrowness of the tube, (*b*) the shortness of the elevated liquid column, (*c*) the difficulty of measuring the mean height of the liquid, (*d*) irregularities in the bore of the tube, and (*e*) the difficulty of securing a clean surface. The method is quite accurate enough, however, for all practical purposes.

Fig. 18 shews the conditions of equilibrium of a liquid which has a smaller tension than that of the material of which the tube is made. A film of the liquid is drawn over the whole of the surface of the bore, and by its tension the liquid is drawn up until it just balances the weight of the column. A very simple calculation gives the superficial tension of the liquid. If r_0 be the radius of the tube, ρ the density of the liquid, g the force of gravity, and h the mean height attained in the capillary tube, the vertical force $(W) = 2\pi r_0 T$ . . . . (6)

This supports a weight of liquid $(W) = \pi r_0^2 h\rho g$ . . . . (7)

consequently $2\pi r_0 T = \pi r_0^2 h\rho g$ (8) ; and $T = \frac{r_0 h\rho g}{2}$ . . . (9)

This method only holds true when the liquid has a smaller superficial tension than the solid, and spreads over it. But there are bodies, such as mercury and glass, where the liquid has in all probability a greater surface tension than the solid. In such an instance, although the liquid adheres with some force to the solid, it cannot spread over it, and the solid on account of its rigidity cannot spread over the liquid, we, consequently, have the combined effects of three tensions to deal with as shewn in fig. 14. The vertical component in this case may act downwards, and the tension of the surface of the meniscus where it touches the glass acts at an angle. But no known lubricants have greater superficial tensions than has glass, and, consequently, although such cases are interesting to physical students, they have little if any practical importance.

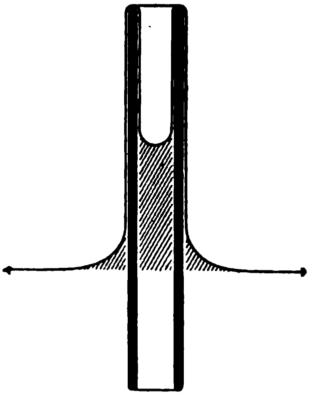

FIG. 18.

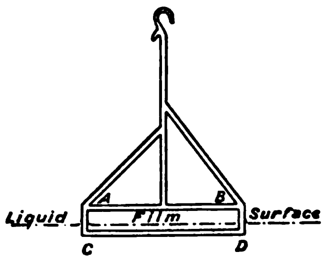

FIG. 19.

By Film Tension.—A direct method of measuring the strength of the tension has been employed by Proctor Hall* at the suggestion of Prof. Michelson.

A glass frame, fig. 19, is suspended from one arm of a delicate balance, so that it is partly immersed in a liquid. The weight is first taken when a film of the liquid is extended between the bar A B and the liquid. The lower bar is completely immersed and serves to stiffen the end portions which dip into the liquid. After breaking the film another reading is made, care being taken that the frame remains immersed in the liquid to exactly the same depth as before. Such a film consists of two surfaces which have closed together and looped round the bars of the frame. The surface tension is the difference between the two weighings divided by twice the width of the frame. When *very* exact determinations are required a small correction has to be made for the width of the frame, for the film distorts the capillary rise of the liquid on the inside of the vertical bars A C, B D. The amount of this correction is found by taking the tension of the same liquid with two or more frames of the same thickness, but of different widths.

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* *Phil. Mag.*, November 1893.

Fig. 20 shews in section the conditions when there is a film in the frame. The tension that may exist on the face separating the liquid from the frame has no effect whatever on the balance, for the surface where the air and the liquid meet encloses the upper bar and closes together to form a film beneath it. This film it is which supports the mass of liquid which is shaded and which acts upon the balance.

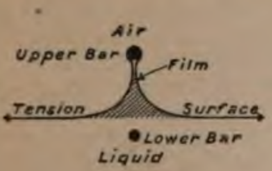

FIG. 20.

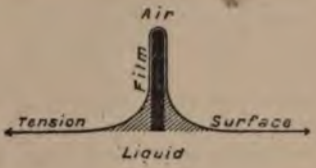

FIG. 21.

By Wetted Plate.—The films of some liquids, such as alcohol, ether, and chloroform, break almost immediately they are formed, consequently their superficial tensions cannot be found by this method. Proctor Hall, therefore, adopted a modification of Wilhelmey's method. The glass or metal frame was replaced by a thin rectangular plate of glass, mica, or metal. The plate was adjusted by trial over a liquid until the whole edge seemed to enter the liquid at once when lowered into it, and when raised slowly parted from the liquid first at both ends and lastly at the middle of the lower edge.

Fig. 21 shews in section the conditions obtaining. The tension surface, separating the air and the liquid, rises over the solid and envelops it, and by its contractile force draws up the two shaded masses of water, the weight of which the balance measures. The results are obtained as follows:—The index of the balance is brought to zero. The vessel containing the liquid is then slowly raised until the liquid touches the under edge of the plate and wets it. As soon as this takes place the liquid film spreads over the plate and by its tension acts on the balance. The balance is again adjusted to zero and the lower edge of the plate is thereby also brought to its original level. Where b is the breadth, τ the thickness of the plate and T the surface tension

$$W = 2(b+\tau)T \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Both these methods give concordant results and admit of extremely accurate work.

Instead of a plate a vertical tube may be slung from a specific gravity balance, the vessel containing the liquid resting upon a table which can be raised and lowered by a rack. Making W the weight on the balance, r_1 the inside and r_2 the outside radius of the tube, then

$$W = T(2\pi r_1 + 2\pi r_2) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$= T = \frac{W}{2\pi r_1 + 2\pi r_2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In other words the weight divided by the inside circumference plus the outside circumference gives the surface tension.

For a description of this and other methods of measuring superficial tension the paper by Proctor Hall* should be consulted.

In all cases the surface tension of the liquid to be measured must be less than that of the solid plate or frame, or the former will not spread over the latter and form a film acting in a direction parallel with the solid surface. A little grease or oil on the plate will so reduce the superficial tension of the solid that water will not spread over it. In all cases the solid should be well washed with caustic soda solution, well rinsed in clean water, and then heated in a Bunsen flame.

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* *Phil. Mag.*, November 1893.

CHAPTER IV.

THE THEORY OF LUBRICATION.

Lubrication and Friction.—*Lubrication of Surfaces.*—In Chapter I. the subject of solid friction was dealt with in some detail, and it was pointed out that unless solid surfaces be contaminated by lubricating substances they generally seize and abrade each other even under very small loads. Such contaminated surfaces cannot properly be called lubricated surfaces, for the particles of the lubricant are merely entangled in the minor surface irregularities of the solid, while still leaving it rough.

The laws of solid friction appear to be unaffected by the presence of contamination films, which only serve to reduce the coefficient of friction and enable metals which would otherwise seize to work together at moderate pressures. On the other hand, when a surface is properly lubricated it is *flooded* with the viscous or plastic substance, and the coefficient of friction depends chiefly upon the nature of the lubricant and the form of the surfaces. Although the difference between a contaminated and a lubricated surface is only one of degree it is convenient to consider surfaces which have been wiped clean as contaminated only, and surfaces which are *wet* with the lubricant as lubricated.

Objects of Lubrication.—In the design of machinery, the engineer seldom has to deal with unlubricated rubbing surfaces. His object is the transference of energy, and its utilization at some particular place, with as little loss as possible. In effecting this the relatively moving surfaces are often pressed together with considerable force, and caused to slide over each other at high velocities. Unless such surfaces be kept apart by the interposition of a lubricant, the frictional losses will be great, and the wear and tear of the surfaces, in most instances, proportionately serious. Indeed, were it not for the properties certain liquids and soft solids possess of keeping the relatively moving surfaces apart, and thereby reducing the frictional resistances between them, it would be impossible to carry on many most important manufacturing processes, or to move our vehicles at anything like railway speeds. In the case of properly lubricated bearings the laws governing the friction between contaminated surfaces do not hold true, for at high speeds and often at comparatively low speeds also, such well lubricated surfaces are wholly separated from each other, and the friction depends upon the thickness of the lubricating film, the area of the surfaces in contact, their relative velocities, and the viscosity of the lubricant.

Theory of Lubrication.—Until quite recently the engineer has had to be guided almost wholly by experience in the design of bearing surfaces and the methods of their lubrication: the theory of lubrication, or of the action of viscous or plastic substances in diminishing friction between relatively moving solids, having received little attention. Not that experimental investigations had been neglected; as a matter of fact a vast amount of experimental data had been collected, but the results not only failed to agree with each other, but they also failed to agree with the general experience of engineers concerning the frictional resistances of machinery. The experiments of Mr. Beauchamp Tower, undertaken at the instance of the Institution of Mechanical Engineers,* have, however, helped to explain the reason of most of these discrepancies. He proved that a great deal depends upon the way in which the lubricant is applied to the bearing: the friction depending upon the quantity and uniformity of distribution of the oil as well as upon the form of the bearing, speed, etc. Most of his recorded experiments were made in such a manner that the lubrication was what he called "perfect": i.e., the bearing was flooded with oil. The results were comparable with each other, agreed better than previous experiments with the frictional resistances met with in such complex machines as steam engines, and were in close agreement with hydrodynamical theory. Taken in connection with other experimental results, they have, thanks mainly to the work of Prof. Osborne Reynolds, enabled us to frame a fairly complete theory of high speed lubrication.

Unfortunately, the same cannot be said of our knowledge of the static or low speed friction of lubricated surfaces. On this subject we can only point out those conditions which seem to be of importance, and give such experimental data as are available.

The theory of high speed lubrication is based upon the supposition that a lubricant acts in virtue of its viscosity and density, physical properties which cause the fluid lubricant to insinuate itself between the relatively moving surfaces and force them apart. Such fluids, however, offer considerable resistance to shear, and, except at low speeds, it is this resistance which mainly occasions the friction of the bearing. The value of this resistance depends upon the viscosity of the lubricant, the relative speed of the surfaces, their area and inclination to each other, and also upon the thickness of the lubricating film at each point. When these conditions are known, the resistance offered to their relative motion can, very approximately, be calculated. That these are really the conditions which determine the friction will be seen when we come to consider bearings of different kinds and compare the experimental results with those deduced from theory.

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* *Proc. Inst. Mech. Eng.*, 1883, 1885, 1888, 1891.

Frictional Losses.—The full benefit derived from the use of a lubricant was, until quite recently, seldom taken practical advantage of, as certain adverse conditions almost invariably accompany perfect lubrication. When the mechanical problems to be solved become better known, such defects will no doubt be capable of remedy. In this connection Prof. J. Goodman* remarks "out of every ton of fuel consumed for engine purposes, some 400 to 800 lbs. are wasted in overcoming the friction of the working parts of the motor, and further, every machine driven by a motor also wastes a large percentage of the remaining power by its own friction. One would not be far short of the mark in saying that from 40 to 80 per cent. of the fuel is consumed in overcoming friction. This extremely wasteful state of affairs is most unsatisfactory, and happily can be greatly improved by a due observance of the laws of friction and lubrication."

Conditions of Lubrication.—Bearing surfaces are of various shapes, the most common form being cylindrical; often, however, they are true planes, but whether cylindrical or flat, the opposing surfaces when working are seldom quite parallel to each other. To illustrate the theory of lubrication, we will take the three following conditions under which a lubricant works in practice:—

1. Static Lubrication.
2. Low Speed Lubrication.
3. High Speed Lubrication.

This order of treatment is convenient as, although at high speeds the friction depends very greatly upon the shape of the surfaces and the free supply of the lubricant, such is not the case at low speeds, for the surfaces then act as though they were approximately parallel, and the lubricating films very thin in places.

Static Lubrication.—*Friction of Thin Lubricating Films.*—When two surfaces, between which there is a viscous lubricating fluid, are pressed firmly together, the lubricant is slowly expelled, the faces eventually approach each other very closely, and in order to cause them to slide over each other, considerable force has sometimes to be exerted. It is evident that if the solid surfaces were perfectly smooth, and the film had an appreciable thickness, any force however small would cause relative motion; for in the case of a viscous fluid film (see p. 19 (5))

$$F = \eta \frac{v_1 ab}{r_0} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the resistance F being proportional to the speed v_1, so that when $v_1 = 0$, $F = 0$.

But bearing surfaces are never perfectly smooth, and, as in the case of so-called solid friction, the projecting portions interlock somewhat, even though they may be prevented from actually touch-

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* Paper read before the Manchester Association of Engineers, March 1890.

[illegible]

[illegible]

[illegible]

[illegible] greater than [illegible] when the load is not [illegible]

[illegible] When the lubricating film is a plastic substance, [illegible] such a film cannot [illegible] by pressure and under ordinary working conditions [illegible] the metallic surfaces never actually [illegible]

[illegible] will be seen from fig. 10, p. [illegible]. The two surfaces A B and C D are approaching without tangential [illegible] the plastic lubricant is being expelled from between them by the pressure set up. The load urging the plates together remaining the same, the thickness of the film decreases until those portions of the lubricant the stresses upon which are sufficient to [illegible] have been expelled. Further approach is then arrested.

Such a film offers, however, a measurable static resistance to shear.

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* *Friction and Lost Work*, p. [illegible]

From experiments made with plastic lubricants (see p. 63) it would appear that under such loads as are used in practice, and when the surfaces are relatively at rest, the film is so thick that the static coefficient is much less than that given by even good viscous lubricants, and also that the coefficient of friction when the speed is small decreases steadily with decreasing speed until the static coefficient is approximated.

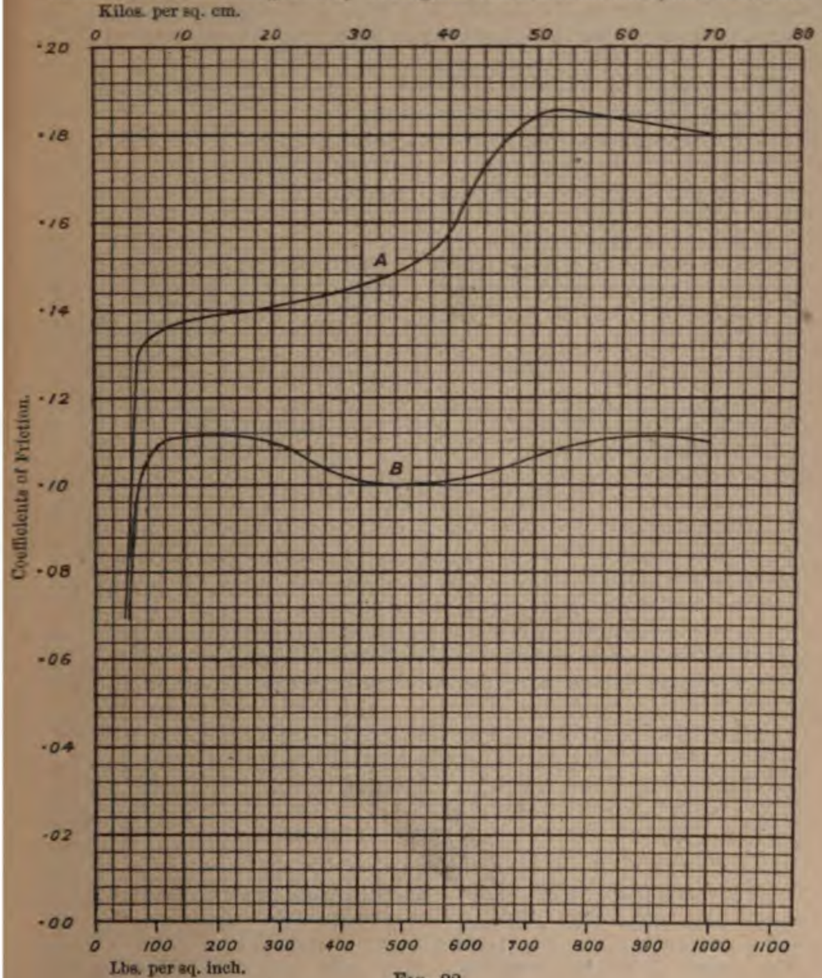

FIG. 22.

Effects of Superficial Tension.—Even when liquid lubricants alone are used, and the pressures forcing the faces together are not too great, the liquid film is only partially expelled, and the irregularities of metallic faces are, to some extent, prevented from interlocking or from cutting or abrading each other when set in motion. Different lubricants form films of very different degrees of thickness. The property does not seem to be in any direct way related to viscosity, for equally mobile liquids vary greatly in their power of forming thick stable films and reducing friction. Although this subject has been already dealt with at some length in an earlier chapter, we will again refer to a few of the main points which seem to have a bearing upon the static coefficient of friction.

Mineral, unlike animal and vegetable oils, seem for the most part deficient in this property of forming thick, permanent films. When used for bearings which have to carry comparatively heavy loads on small rubbing surfaces, mineral lubricants are therefore often mixed with animal or vegetable oils, greases, fats, etc. The power a liquid film possesses of resisting complete expulsion from between two metallic surfaces may be regarded as due to two causes. In the first place, there is the interfacial action which causes oils to spread themselves over metallic surfaces. Lord Rayleigh has shewn that when several liquids are brought into contact with a solid whose surface tension is greater than that of either of them, the conditions of equilibrium or of minimum potential energy are satisfied when the liquid of greatest surface tension is in contact with the solid, and the other liquids assume the order of their relative surface tensions.

Water, however, although it has a greater surface tension, cannot, as a rule, displace oils, greases, fats, etc., from the surfaces of solids, for such substances are insoluble in water and insinuate themselves among the surface molecules or atoms of the solid, from which they are not easily separated. When the temperature is high, and the surfaces abrade each other, water is apt to displace the lubricant and seriously increase the friction coefficient. Water arising from condensation in the steam pipes, etc., interferes seriously with the proper lubrication of the valves, piston rings, etc., upon which it is apt to be deposited.

All lubricants have smaller surface tensions than the solids between which they are used, consequently they readily spread over and wet such surfaces. Were it not for this action it would be impossible to apply the lubricant in many of the ways now commonly employed.

But in addition to this power of spreading over, or *wetting*, metallic surfaces, note must be taken of the power certain films possess of resisting *disruption*. For instance, a film of pure water ruptures almost immediately it forms. Such a film consists of two surfaces, in each of which the molecules are in a peculiar condition of stress. When the marginal molecules of the two surfaces meet, the film becomes locally weak and ruptures. The addition of a little soap, although it reduces the surface tension of the film by nearly one-half, causes it to persist and strongly resist rupture at points where it has become thin.

Dr. Dupré and Lord Rayleigh proved that, at the moment of their formation, surfaces of soapy water have hardly less surface tension than pure water. The soap in the film is slowly evolved from the interior, and not only alters its tension and prevents it from rupturing but also increases its viscosity. Clean water supplied to hydraulic machinery has little or no lubricating effect upon the bearing surfaces of valves and other moving parts, which when unlubricated abrade each other very rapidly. A little soap added to the water makes all the difference. The film *resists rupture*, feels 'soapy' between the fingers, becomes more viscous, and keeps the metallic surfaces from abrading each other.

Owing to the concentration of the soap in the surface film, only a very small quantity is required to secure the proper lubrication of hydraulic valves, etc.

The result produced by the varying thicknesses of the permanent greasy films of different lubricants has already been seen, as regards sperm oil and lard oil, in the case of the static friction coefficient. But as its value in lubricating problems is most marked when the speed is low and the loads high, detailed reference to it is convenient at this juncture.

Low Speed Lubrication.—*Conditions of Lubrication.*—At high speeds we shall find that with some kinds of bearings the lubricant becomes trapped in considerable volumes between the opposing relatively moving surfaces, and as it cannot escape freely again, the surfaces remain completely separated by a viscous film. At very low speeds, however, this is not the case, and if the load be too great, or the rubbing surfaces are of unsuitable materials, there is danger of so cutting and tearing the bearings that they will run hot. Static friction and low speed friction effects are, indeed, of great importance in almost all cases, for machines have generally to be started from rest with considerable loads on the bearings. This is especially the case with the axles of railway vehicles, the journals of which require very careful lubrication; endurance and a low coefficient of friction being of paramount importance. Turntable centres, the motion pins of slowly moving engines, etc., and indeed the friction of the rubbing surfaces of all kinds of slowly moving machinery, is largely dependent upon the nature of such surfaces, the greasiness or oiliness of the lubricant used, the viscosity of the oil, and the rate at which the viscosity decreases with rise of temperature.

The irregularities of even smooth rubbing surfaces, although they may be separated over considerable areas by continuous films of the lubricant, often actually engage each other at numerous points. At such places abrasion occurs, often without serious results, for the liberated heat can, in most cases, pass freely away, and the lubricating film is not permanently broken. Should, however, the materials forming the bearing surfaces be such that when forced into contact they readily weld together, the surfaces may seize completely over large areas. Therefore, although at all ordinary running speeds the friction depends almost wholly upon the action of the lubricant, and very little, if at all, upon the nature of the surfaces in contact, it cannot be too clearly understood that, at low speeds and with heavy loads, this is by no means the case, and that so much injury may be done at starting that, even if the surfaces do not seize, the liquid film cannot be properly formed between the uneven surfaces at high running speeds, and the friction, owing to the formation of a thin film of irregular thickness, becomes so great that undue heating results.

The effects at low speeds are practically the same whether the surfaces be plain, cylindrical, or of double curvature. In this respect again the laws of low speed friction differ from those obtaining at high speeds, for at high speeds the magnitude of the coefficient depends upon the shape of the surfaces as well as upon the nature of the lubricant, etc.

The great frictional resistance met with at low speeds is well known to all who have noticed heavy machinery running slowly, or who have seen hydraulic pumping engines start from rest. In the latter case, from the moment the engine commences to move it has to deal with the full load on all its bearings. In consequence of this all the faces are firmly pressed together, and the lubricating film, especially if it be a mineral oil, is not sufficiently thick to prevent even the minute irregularities of the surfaces from interlocking somewhat, and the bearings often 'groan' and the parts move by jerks. But as the speed increases this jerky motion decreases, the machinery 'groans' less and less, and finally moves easily and noiselessly. At the lower speed the lubrication is imperfect, but by the time the relative speeds of the rubbing surfaces have reached 10 or 20 feet per minute, comparatively thick films of oil have been thrust by the motion of the shafts, etc., between them and their bearings, and the load is carried by oil films only. When this comparatively thick film has formed and the faces either wholly or over the greater part of their surfaces have separated, the lubrication is said to be 'perfect.'

Metals for Bearing Surfaces.—Owing to the fact that at low speeds the opposing surfaces may actually abrade each other, it is customary to make the metal of one of the surfaces of some alloy which will not easily adhere to, and is much softer than, the opposing metal. Magnolia metal, Babbit's metal, various white metals, brasses and bronzes, are much in demand for bearing surfaces to work in contact with steel or iron. The effects resulting from the actual contact of the surfaces have been considered in Chapter I., and need not again be discussed here. However, the necessity of choosing suitable metals to run upon each other cannot be overrated.

Influence of Viscosity.—The influence of the viscosity of the lubricant shews itself from the moment the surfaces commence to move relatively to each other, and becomes more and more marked as the speed increases. The effect upon the coefficient of friction at low speeds is in a great measure dependent upon the roughness of the surfaces and the disposition of the oil ways. The film maintained by the action of irregularities is often very thin indeed, and must not be confounded with the *pressure film* which forms at high speeds (see p. 64), and to which perfect lubrication is due.

Coefficient of Friction at Low Speeds.—The friction is much less dependent upon the system of lubrication at low speeds than at higher speeds; indeed, with a short chord of bearing surface, and therefore with heavy loads per square inch, the friction is approximately the same whether the pad, oil-bath, or other system of lubrication be adopted. The following results were obtained by Goodman*:—

TABLE V.—COEFFICIENT OF FRICTION AT A SPEED OF 7·8 FEET PER MINUTE.

System of Lubrication.	Length of Chord of Bearing Surface (inches).				
	2·0	1·75	1·5	1·0	0·5
	Coefficients of Friction.				
Oil Bath . . .	0·92	0·70	0·64	0·48	0·47
Saturated Pad . .	1·13	0·92	0·72	0·48	0·46
Oily Pad . . .	1·87	1·25	0·94	0·57	0·51

At one time it was supposed that there was always a sudden change in the value of the coefficient of friction when the surfaces in contact came relatively to rest. This was shewn to be erroneous by Profs. Jenkin and Ewing,† who found that although the frictions of rest and of motion have often very different values, in no instance was there a sudden or abrupt change in value, the kinetic coefficient gradually changing as the speed decreased until the static coefficient was reached. Their object was to measure the friction at such low velocities as 0·0002 feet per second, and from the results they obtained, we may safely conclude that the coefficient gradually changes when the velocity becomes small, so as to pass without discontinuity into the friction of rest.

Subsequent experiment has amply confirmed this view. Still our knowledge of the variations which the kinetic friction undergoes with change of speed is by no means complete, few experiments having been carried out at very low velocities. Profs. Jenkin and Ewing employed very considerable loads, and their bearing surfaces were spindles resting upon flat surfaces. These conditions were found by Prof. Kimball to favour a coefficient decreasing continuously with increase of speed.

Profs. Jenkin and Ewing state that in the case of brass, the coefficient was found to be ·146 at all speeds from ·0002 to ·0064 feet per second. In the case of steel upon steel, however, the coefficient increased from ·119 at ·0002 feet per second to ·13 at ·0046 feet per second. This increase, and also a subsequent decrease of the coefficient of friction with increasing speed, is much more clearl brought out by Prof. Kimball. He describes the contrivance l used as follows:—

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* Goodman, *Friction and Lubrication of Cylindrical Journals* (pamphlet), 1890, p. 133.

† *Phil. Trans.*, 1877, p. 509.

"A shaft one inch in diameter was adjusted so that it could b driven at almost any rate between one revolution in two days and thousand in a minute. A hole was bored through a block of ca iron 3½″ × 3½″ × 1½″ and carefully fitted to the shaft; rigid iro rods were screwed into the top and bottom of this block, and adjuste so as to stand in a vertical line at right angles to the shaft. Upo these rods slotted weights could be placed, and thus the pressur upon the shaft and the centre of gravity of the brake could b readily adjusted."

The two following tables give the results obtained:—

TABLE VI.

FEET PER MINUTE.	CM. PER SECOND.	RELATIVE VALUES OF CO-EFFICIENT OF FRICTION.
·00058	·000295	0·37
·00225	·001144	0·51
·00500	·002540	0·73
·01100	·005590	1·00

These results shew a coefficient *increasing* as the velocity increase

TABLE VII.

FEET PER MINUTE.	CM. PER SECOND.	RELATIVE VALUES OF CO-EFFICIENT OF FRICTION.
6·0	3·05	1·00
22·6	11·49	0·60
50·4	25·61	0·46
110·0	55·90	0·29

These results, unlike the former, shew a coefficient *decreasing* the velocity increases.

The view held that the coefficient of friction of lubricated bearin at very low speeds is often greater than the static coefficient is su ported by many other facts. Prof. Goodman's experiments (Tab VIII. p. 61) may be instanced. On the diagram, fig. 23, the curve shews the manner in which, in these experiments, the friction vari at moderately low speeds with a load of 150 lbs. per square inch. the curve A were continued so as to cut the ordinate of no spee the static coefficient would be about 0·21. This is for bath lubricati —with saturated pad lubrication (curve B) the static coefficie

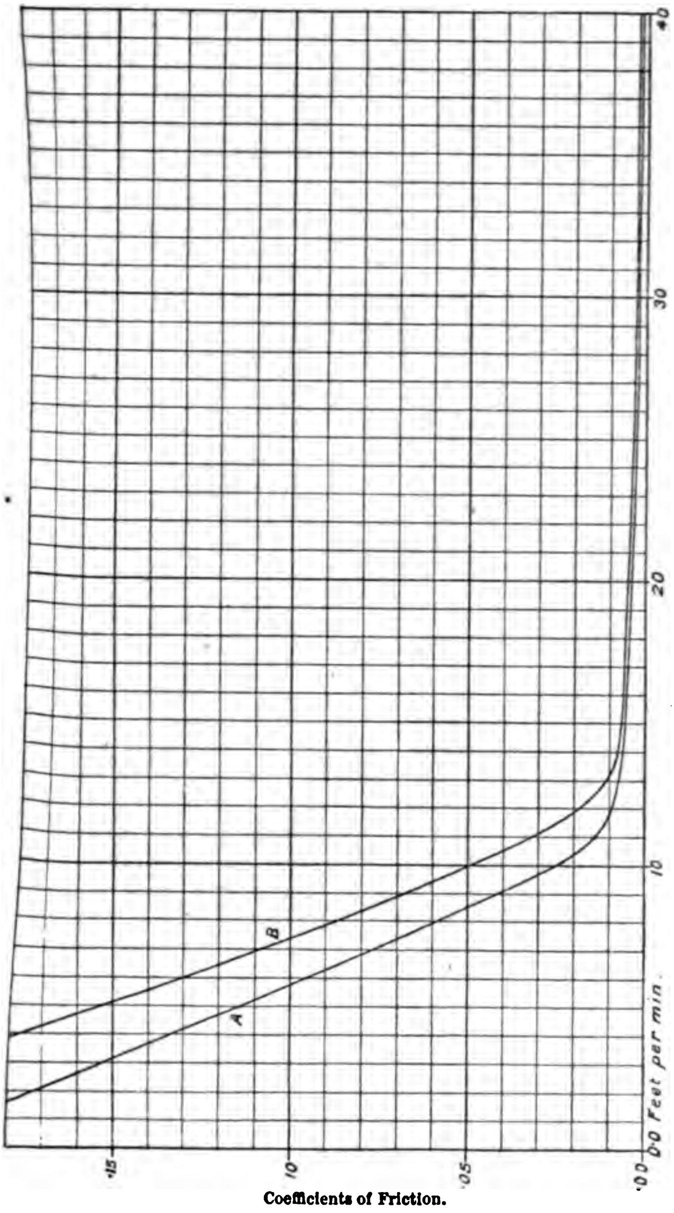
·15
·10
·05
·00
0·0 Feet per min.
10
20
30
40
A
B
Coefficients of Friction.

FIG. 23.

would be about 0·27. These are high figures when compared with the static coefficients obtained by Thurston, which are given on diagram, fig. 22. It is probable that had Goodman experimented at much lower speeds, he would have found that the friction assumed a maximum at a comparatively low velocity, and then decreased again as the speed decreased. Wellington's results[*] were obtained by noting the resistance offered to the motion of wagons, and cannot be considered as accurate measures of journal friction at very low speeds, as the resistance was partly due to the *rolling* friction of the wheels on the rails, vibration, etc. With lubricated journals it would appear that the coefficient of friction is at a maximum at some speed below one centimetre per second. Kimball[†] says that an increase in the pressure between the surfaces in contact changes the value of the maximum coefficient, and makes it correspond to a smaller velocity. The more yielding the materials between which the friction occurs, the higher is the velocity at which the maximum coefficient is found. Heating the bearings changes the position of the maximum coefficient to a higher velocity. In the vicinity of the maximum coefficient, the friction generally remains sensibly constant for a considerable range of velocities. With speeds above one centimetre per second, or thereabouts, a viscous lubricant being used, the friction of journals falls rapidly until a velocity of about five centimetres per second is reached. The friction then increases very slowly to the highest speeds at a rate depending upon the method of lubrication employed. This change of the coefficient of friction with increasing speed is shewn on the diagram, fig. 24. From *a* to *b* the curve rises, indicating that at the lowest speeds, below one centimetre per second, the coefficient of friction increases with increasing speed. With further increase of speed, the coefficient of friction rapidly decreases and reaches a minimum (at *c*), if the lubrication is good, at a speed of about five centimetres per second; it then slowly increases again. With imperfect lubrication, or with plastic lubricants, the coefficient of friction falls less rapidly from *b*; indeed, the speed may reach 100 feet per minute before the lowest point *c* of the curve is reached.

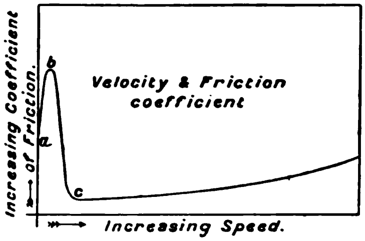

FIG. 24.

In Table IX. (p. 70), which will be fully described later, the value of a certain constant, C, leads to the belief that, as in the case of cylindrical surfaces, the lubrication of plain surfaces is also imperfect at low speeds and with heavy loads. When the value of C ceases to vary the pressure film has, there is every reason to believe, established itself.

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[*] *Trans. Amer. Soc. Civ. Eng.*, 1884.

[†] *Amer. Journ. Science*, 1876.

a mean speed of about 60 feet per minute, and with greater than 60 lbs. per square inch, the pressure film is partly *crushed* nd the friction becomes abnormally great, as shewn by the large increasing value of C. At 90 revolutions per minute, even 160 lbs. square inch is satisfactorily carried, but at speeds below 13 feet minute even with 20 lbs. per square inch the pressure film is not erly formed and the friction is high.

TABLE VIII.*—CHANGES IN VALUE OF THE COEFFICIENT OF FRICTION WITH INCREASING SPEED.

SPEED. eet per Minute.	Coefficients of Friction (μ_1) under a Pressure of		
	50 lbs. per sq. in.	75 lbs. per sq. in.	150 lbs. per sq. in.
5	...	·0025	·1145
10	·0009	·0007	·0250
15	·0012	·0008	·0051
20	·0014	·0009	·0034
25	·0017	·0011	·0027
30	·0021	·0013	·0023
40	·0026	·0016	·0019
50	·0032	·0018	·0017
70	·0042	·0024	·0017
90	·0053	·0030	·0020
110	·0064	·0036	·0024
130	·0075	·0042	·0029
150	·0086	·0048	·0035
170	·0096	·0054	·0041
190	·0106	·0060	·0047

n the case of a journal the high coefficient of friction at low speeds lso very striking, especially when the load per square inch is iderable. Table VIII. shews the changes in the value of μ_1 with easing speed when the pressure is 150 lbs., 75 lbs., and 50 lbs. square inch, and the lubrication 'perfect.' With the smaller load, at such a speed as 10 feet per minute, the coefficient of friction nall. At 75 lbs. per square inch the friction is at a minimum be- n 5 and 10 feet per minute, whilst at 150 lbs. per square inch minimum frictional resistance is not reached until a speed of t 40 feet per minute is attained. In other words, the lubrication, pt with small loads, is imperfect at low speeds, a high speed being ired to form a sustaining liquid pressure film.

lthough the above statements concerning the changes the low d friction undergoes with slight changes of speed are doubtless ect for certain conditions, the effects produced by changes in the osity and other properties of the lubricant, the method of its ap-

These figures have been obtained by plotting the values given in Goodman's s.

[illegible] the rubbing surfaces, are [illegible] the action of a lubricant in [illegible] are small been sub- [illegible] mathematical treatment. [illegible] such circumstances can be [illegible]

[illegible] have already pointed out [illegible] the friction [illegible] low speeds: indeed [illegible] were sufficiently [illegible] We may therefore [illegible] compared with the [illegible] as the speed increases [illegible]

[illegible] which shews an en- [illegible] prevented from [illegible] As the surfaces move over [illegible] the elevated portions [illegible] approach and recede, and the greater the relative speed the [illegible] is this action. Each [illegible] points as A and B approach the liquid is expelled from between them, and then drawn in again as they recede from each other. [illegible] viscosity of the lubricant resists this [illegible] of the film more and more [illegible]

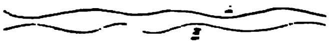

Fig. [illegible]

[illegible] the smaller is the volume of lubricant [illegible] between the asperities, and the thicker the film [illegible]. Even at very low speeds this thickening of the film [illegible] at the front edge of the [illegible] at a later stage, as to it must [illegible] of even flat surfaces at high speeds. The thickening [illegible] by the asperities passing over each other can only occur to a very limited extent, and would seem to prevent the kinetic friction at [illegible] speeds from exceeding the static friction by so much as it otherwise would.

The resistance due to the viscous friction of the film is proportional to the speed of rubbing, and inversely proportional to its thickness. Up to speeds somewhat below one centimetre per second we must therefore assume that the lubricating film does not thicken with sufficient rapidity to prevent the speed from increasing the frictional resistance. At greater speeds, however, the film thickens so rapidly, as compared with the increase in speed, that the coefficient soon falls to a small fraction of its original value.

Within certain limits, the smoother the surfaces the smaller the static coefficient; but at very low speeds such surfaces give comparatively high frictional resistances, for the films are then exceedingly thin, and are not increased much by the action above described.

Lubrication with Plastic Solids.—For a number of years 'greases' were almost exclusively used for railway axles. They are generally emulsions of water, tallow, and some vegetable oil, with sufficient alkali to neutralize the acids and form soaps. Such axle greases are plastic rather than viscous compounds, and require the exertion of a certain definite pressure to cause them to flow. Owing to this fact they cannot be completely squeezed out from between the brass and its bearing. They are, on the other hand, readily forced in at the higher velocities. Although offering much more resistance to motion at high speeds than does a lubricant of low viscosity, the much greater thickness of the plastic film, when the speed is low, makes the static friction less than is given by most, if not all, truly viscous fluids. On this account, although the friction of a rapidly moving train lubricated by oil may be much less than when plastic greases are used, a much greater force is required to set the coaches in motion. Greases have consequently maintained their position as lubricants for low speed goods trains on most lines.

Mr. T. G. Clayton* has made an exhaustive series of experiments to ascertain the friction of a number of coaches belonging to various railway companies with a view to measuring the static friction when using oil and grease respectively as lubricants. He found that on the average a tractive force of 12·62 lbs. per ton was required to move a coach when lubricated with grease, whereas a force of 18·54 lbs. per ton was required when oil was used.

To keep the rubbing surfaces of bearings from coming into contact, owing to the expulsion of the lubricant by the load, when their relative velocities are small, oils, waxes, and greases containing solid lubricants are much more extensively used than are solids alone. As a rule, the viscous or plastic matrix acts as a carrier for the solid lubricant, and enables it to be more readily applied to the rubbing surface. It is placed in such a position, with regard to the bearing, that should the liquid lubricant be rubbed out, the heating arising from the increased friction melts the matrix, and the mixture, containing the solid, immediately runs on to the dry surface.

Such compounds are mostly suitable for heavy pressures and low speeds. At high speeds their frictional coefficient is very great, and the heating and loss of power they cause is proportionately serious. Their use is therefore almost entirely restricted to bearings which are only in motion occasionally, or to such bearings as the journals of tip wagons, or the axles and spindles of hauling machinery. The solid portion of the lubricant finds its way into the surface irregularities and fills them up, thus increasing their smoothness. It also prevents the metals from welding to each other, at points where they are brought into contact by excessive pressure. Solid lubricants are often mixed with liquid ones and used for rubbing surfaces which have not properly worn themselves true, for although the coefficient of friction may be high, and the bearings become heated, the solid lubricant prevents the injury that would otherwise result from the decreased viscosity of the liquid. Thus graphite, soapstone, and paraffin wax melted together and worked, while hot, into a plaited rope of cotton, jute or hemp, constitute an excellent packing for piston rod and other glands. The wax keeps the packing soft and pliable, the soapstone and graphite serve to make it durable, whilst the fibrous material binds the whole together and gives it a form convenient for the user.

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* *Lubrication and Traction relating to Railway Carriages* (pamphlet). William Clowes & Sons, 1892.

High Speed Lubrication.—*Lubricating Film.*—At a speed depending greatly upon the load and the nature of the lubricant, the rubbing surfaces commence to separate, and a comparatively thick *pressure film* forms between them and carries the load. The extent to which the thickness of this film increases with the speed varies not only according to the load, the viscosity of the lubricant, the area of the bearing, and the speed, but also according to the shape of the surfaces and the relative positions they assume. As illustrations of the conditions under which pressure films are produced, and those which determine their thickness, it will be convenient first to consider the case of plane parallel surfaces, then of plane surfaces inclined to each other, and finally of cylindrical surfaces such as those of journals.

*Lubrication of Plane Parallel Surfaces.**—Although neither a very common form of bearing nor one that will carry very great loads, the conditions which obtain when plane parallel surfaces are pressed together, and caused to slide over each other, are of considerable interest, for the laws which govern the frictional resistance in such cases serve to illustrate very clearly the mode in which viscous substances reduce the friction between relatively moving bodies.

The subject was one that engaged the close attention of Mr. Beauchamp Tower. Indeed, had it not been for his experimental work, to which reference has already been made, we should have been without the data upon which to found a hydro-dynamical theory. Of the experiments made by Mr. Tower those on pivot friction have most bearing upon the subject in hand.

In these experiments, faces which were free to move to or from each other were constrained to remain parallel. The pivot experimented with was of steel, had a perfectly flat end 3 inches in diameter, and was pressed against a manganese bronze bearing in such a manner that the faces, although they could separate, were always parallel to one another. The exact form of bearing and the details of the machine employed are given in another place. The lubricant was supplied through a hole in the centre of the bearing, and was distributed by two radial grooves extending from the centre hole to within a $\frac{1}{16}$ of an inch of the periphery of the bearing surface. In this way the bearing was always kept flooded with oil, which remained clean and bright during the experiments, indicating that no abrasive action was taking place. In other words, the lubrication was 'perfect,' *i.e.*, there was a comparatively thick film of oil maintained under pressure between the surfaces, which were thus prevented from touching each other. To the viscous action of this oil film the friction was wholly due, being smaller the thicker the film, and greater the higher the speed. However, with each change of speed or load a corresponding change in the thickness of the film took place, and, therefore, of the frictional resistance also.

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* Deeley and Wolff, *The Engineer*, 10th January 1896, p. 25.

Fig. 26 illustrates the action of such a film. It shews two parallel planes of unlimited length and breadth separated by a viscous film of thickness r_0. The upper plane CD is supposed to be *fixed*

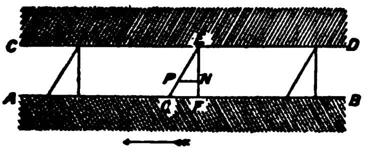

FIG. 26.

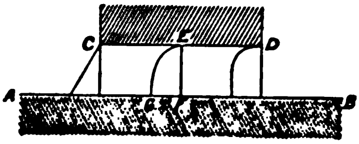

FIG. 27.

while the lower plane AB moves in the direction of the arrow with a velocity v_1. By the definition of viscosity (p. 19) there will be a tangential resistance to motion.

$$f = \eta \frac{v_1}{r_0} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

η being the viscosity of the liquid. When one plane has an area A, the total resistance to motion

$$F = \eta \frac{v_1 A}{r_0} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The tangential motion varies uniformly from v_1 at AB to nil at CD. Thus if the length FG be taken to represent v_1, then the length of the line PN will represent the velocity at P.

When first the planes are set in motion the inertia of the viscous liquid prevents it from at once assuming this condition of flow, but in a comparatively short period all irregularities of motion subside, and the velocity of the liquid at any plane is strictly proportional to its distance from CD.

Inertia effects also shew themselves when one plane is of finite extent. They tend to throw the surfaces apart and maintain a film of the liquid between them. In fig. 27 the surface CD is supposed to be of limited length both parallel with and in a direction perpendicular to the paper. AB is flooded with oil, which when approaching, but at some distance from D, is moving at the speed v_1 of the plane AB. Just before reaching D a relative motion or distortion of the fluid is produced. At D, the oil in actual contact with the fixed plane is at rest, and the remainder, instead of passing along between the surfaces in such a manner that the *rate* of distortion is everywhere the same, as in fig. 26, is caused by its own inertia to enter the space between the planes, and to flow in such a way that—as shewn in fig. 27—the rate of distortion becomes much greater near the plane CD than near the plane AB; whilst at the end C the rate of distortion of the lubricant, in virtue of its viscosity, may have become approximately the same at all planes. Under these conditions, therefore, the lines EG are curved, the rate of distortion is greater near CD than near AB, and the volumes passed at each section are proportional to the areas enclosed by EFG. It will be noticed that these areas are larger at the entrance D than at the exit C, part of the excess of liquid escaping laterally owing to the comparatively small width of the plane CD in a direction perpendicular to the surface of the paper. When the velocity with which the lower plane moves is very small, the volume carried in between the surfaces is nearly proportional to $\frac{EF \cdot GF}{2}$, and at the opposite end of the plane the same volume is carried out: but as the speed increases the volume introduced may exceed the volume carried out at C by an amount almost proportional to $EF \cdot GF - \frac{EF \cdot GF}{2}$

$$= \frac{EF \cdot GF}{2},$$

at which the excess remains unaltered, however much the speed may be increased.

When the planes are of considerable area, and are close together, the viscosity of the oil powerfully resists its escape at all points, and at the same time, by tending to make the rates of distortion everywhere equal, causes it to accumulate and force the planes apart until the forces are in equilibrium. This action is going on at all points between the surfaces when their length, measured in the direction of motion, is not very great. The force tending to throw the planes apart is, therefore, distributed over them much as is the force resisting the approach of two surfaces separated by a viscous medium.

In this way when the opposing surfaces are constrained to remain parallel, a pressure film is maintained between them, and a considerable load may be supported by CD so long as AB is in rapid motion. The resistance to the motion of the lower plane is then due wholly to the viscosity of the liquid film. It is, however, somewhat in excess of the value obtained by the formula $F = \eta \frac{v_1 A}{r_0}$, for owing to the excess of oil introduced at D, the conditions of motion are not exactly those shewn in fig. 26. No correction for this small difference will be attempted.

We will in the first place deal with the conditions determining the volume V, introduced owing to the relative motion of the surfaces and the density of the liquid. The viscous liquid resting upon AB at points distant from the surface CD is moving with a velocity v_1. At the point D, when the velocity is considerable, the liquid is *thrown* against the opening between the surfaces, much in the same way as water from the combining cone of an injector is thrown against the orifice of the delivery cone. Its power of entering the opening may be regarded as proportional to the density of the liquid and to the square of the velocity. It is almost independent of the viscosity; for the entrance of the liquid is as much opposed by its adherence to CD as it is assisted by its adherence to AB.

No doubt, at low speeds, as the load urging the faces together is increased, the volume entering decreases more rapidly than does the distance separating the rubbing surfaces, until finally the marginal pressure of the imprisoned film prevents the liquid from entering at all, and the faces close together; but when the speed is great and the load is increased, there is reason to suppose that the liquid fails quite suddenly to get between the surfaces, which thereupon 'seize.' We may therefore assume that, except at low speeds, the volume entering is approximately proportional to

$$v_1 r_0 b = \mathrm{V},$$

r_0 being the distance between the surfaces, and b the length of the orifice at D.

In the case of a rectangular bearing, the viscous liquid is introduced along one side and escapes along the margin of the other three, and the larger the volume introduced, the more the bearing surfaces part in order to allow it to escape.

The conditions attending the escape of the fluid may, therefore, be well illustrated by taking the case of parallel surfaces approaching each other without tangential motion (fig. 28).* The fluid has to be *squeezed out* from between the surfaces, and since there is no motion of the fluid in contact with the surfaces, the horizontal velocity will be greatest half way between them, nothing at O (the middle of CD), and greatest at the ends. This is for planes of infinite length in a direction perpendicular to the plane of the paper. If in a certain state of motion—shewn by the dotted lines in fig. 28—the space between AB and CD be divided into ten equal parts by vertical lines, and if those lines be supposed to move with the fluid, they will shortly after assume the positions on the curved lines, in which the areas included between each pair of curved lines is the same as in the dotted figure. If it were not for the inertia of the fluid, the lines

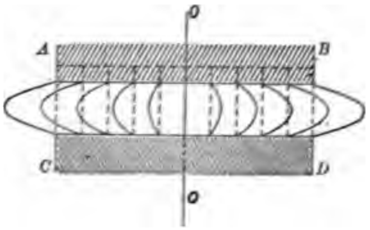

FIG. 28.

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* Osborne Reynolds, *Phil. Trans. Royal Society*, 1886, p. 173.

would be absolute, instead of approximate, parabolas. It can be at once seen that the curved lines indicate the rates of distortion at different points, and, as force is required to maintain the rate of distortion at each plane constant, a vertical pressure W must be applied to force the liquid out. The pressure will be greatest at O, and will fall off towards the ends C and D.

In the case of an ellipse of semi-axes *a* and *b*, it follows from Professor Osborne Reynolds' equations that the velocity of normal approach is proportional to $\frac{r_0{}^3 W(a^2+b^2)}{a^3 b^3 \eta}$.

Therefore the escaping volume may be written

$$V_1 = k\frac{r_0{}^3 W(a^2+b^2)}{a^2 b^2 \eta} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We thus obtain expressions for the volume V of the viscous liquid introduced by the motion of the bearing, and also for the motion V_1 of the liquid pressed out by the weight on the brass. In order that the conditions of flow may remain constant, these two values must be equal, consequently

$$V = V_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$= v_1 r_0 b = k_1 \frac{r_0{}^3 W(a^2+b^2)}{a^2 b^2 \eta} \quad . \quad . \quad . \quad . \quad (6)$$

and

$$v_1 = k_1 \frac{r_0{}^2 W(a^2+b^2)}{a^2 b^3 \eta} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\therefore \quad \frac{v_1{}^2 \eta^2 a^2 b^2}{r_0{}^2} = k_1 \frac{v_1 W(a^2+b^2)\eta}{b} \quad . \quad . \quad . \quad . \quad (8)$$

The left-hand term of this equation gives us the value of F^2 required to maintain the plates in steady motion, since F (equation 1) is inversely proportional to r_0 and directly proportional to $v_1 \eta a$.

$$\therefore \ F \propto \sqrt{\frac{v_1 W(a^2+b^2)\eta}{b}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which in the case of a circle, when $b = a$, resolves itself into

$$F \propto \sqrt{v_1 W b \eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and as the coefficient of friction (μ_1) is equal to the resistance F divided by the total load

$$\mu_1 = \frac{F}{W} = c\sqrt{\frac{v_1 \eta b}{W}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The values of F and the coefficient of friction will, therefore, vary with the shape of the surface boundary, but will be constant for surfaces of similar shapes. Hence in the case of the circle, ellipse, and rectangle, we see that, the proportions being unaltered, and the premises correct, the friction varies as the fourth root of the area of the surfaces.

Experiment appears to bear out this statement, for it has been found that the coefficient of friction of a pivot or plane surface is affected much less by the size of the bearing than by the velocity at which it runs or by the load which it carries, the pressure film being unbroken.

Although in Mr. Tower's experiments every care was taken to measure the friction between the surfaces, and to keep them in good condition, no attempt was made to ascertain the rise of temperature produced by different speeds and loads, or the value of the viscosity of the oil used. Some resistance to motion must also have been offered by the oil film surrounding the cylindrical portion of the footstep, but as the clearance is not given, and we do not know the viscosity of the oil, its magnitude cannot be calculated.

We are consequently unable to compare one experimental result quite satisfactorily with another.

Assuming that the oil did not vary very much during the trials, and that the cylindrical footstep was a moderately loose fit in the brass, we may write from (11)

$$C = F\sqrt{\frac{1}{NW}} \quad . \quad . \quad . \quad . \quad (12)$$

N being the number of revolutions of the footstep, and C a constant.

In Table IX. are given the values of C, calculated from Mr. Beauchamp Tower's experimental results, the mean speeds of the footstep, the loads, and the frictional resistances. At low speeds C has a high value which increases steadily as the load increases, shewing that the volume of oil entering is not proportional to $EF \cdot GF$, and is not keeping the surfaces properly apart. At higher speeds, however, C actually decreases somewhat until the heaviest loads are reached. The decrease is probably brought about by the heating effect of the friction decreasing the viscosity of the lubricant, or by the fact that the force measured by Mr. Beauchamp Tower was partly due to the viscous resistance of the oil film surrounding the cylindrical portion of the footstep. In all cases the highest loads cause a small increase in the value of C, in spite of the fact that the viscosity of the lubricant must have been lowered by the heat generated by friction. Under these conditions the film would be thin, and the volume of liquid introduced by its inertia, somewhat less than when r_0 is large.

Lubrication of Inclined Plane Surfaces.—As a rule, even when the rubbing surfaces are plane, the opposing surfaces are free to adjust themselves according to the position of the load they carry and the distribution of the pressure of the film keeping them apart. The conditions under which the lubricant acts then differ somewhat from the case of plane parallel surfaces. In the latter case it is to the *inertia* and *viscosity* of the lubricant that we must attribute the presence of the pressure film; but when the faces are free to become inclined, the liquid wedges itself between them and forces them apart. The conditions then obtaining have been carefully considered by Prof. Osborne Reynolds, and merit close attention, as it is to this action that he ascribes the great carrying power of cylindrical bearings.

TABLE IX.—VALUES OF 'C' FROM MR. BEAUCHAMP TOWER'S EXPERIMENTS.

Load.	50 Revs. per Min.		128 Revs. per Min.		194 Revs. per Min.		290 Revs. per Min.		353 Revs. per Min.	
	13·09 Feet per Min.		33·51 Feet per Min.		58·28 Feet per Min.		75·08 Feet per Min.		92·41 Feet per Min.	
Lbs. per sq. in.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.
20	2·77	·087	1·13	·0223	1·44	·0231	2·51	·0294	2·36	·0281
40	4·61	·103	1·54	·0215	1·74	·0197	3·03	·0282	2·72	·0229
60	7·07	·129	2·26	·0258	2·15	·0199	3·33	·0252	3·08	·0212
80	10·25	·162	3·59	·0355	2·56	·0206	3·64	·0239	3·59	·0214
100	15·48	·218	5·48	·0484	3·13	·0225	3·95	·0232	4·00	·0213
120	18·72	·241	7·02	·0566	4·41	·0289	4·10	·0219	4·51	·0219
140	...	...	9·23	·0690	6·10	·0370	4·51	·0224	5·23	·0235
160	...	...	12·82	·0897	7·69	·0427	5·03	·0233	6·15	·0252

As to the frictional resistance and carrying power of plane surfaces such as engine slide blocks which become slightly inclined to each of the faces they run upon, no experimental results have yet been obtained which can be compared as regards accuracy with Mr. Beauchamp Tower's tests of pivot bearings.

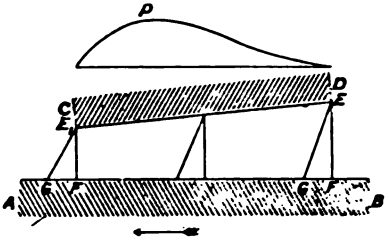

Fig. 29.

In fig. 29 AB is a plane surface of unlimited length and breadth moving in the direction of the arrow beneath the inclined surface CD, which is of limited length and very limited breadth, in a direction perpendicular to the paper. Omitting the effects which would be produced by the inertia of the liquid, the conditions of flow are as follow:—

At the lower edge of D where the liquid enters between the surfaces, the volume introduced is proportional to $\frac{EF.GF}{2}$.

However, owing to the inclination of the surfaces, the volume passed out at the edge C is only proportional to $\frac{E_1F_1.GF}{2}$.

When the surface CD is of considerable area and the planes are very close together, the excess of oil or other lubricating fluid introduced at the edge D must escape; but this is opposed at all points by the viscosity of the liquid. The oil, therefore, tends to accumulate, and a pressure is set up which forces the surfaces apart until the load is sufficient to prevent further recession. In this respect the action is similar to that we have already described as resulting from the inertia of the entering fluid.

According to Prof. Osborne Reynolds the effect reaches a maximum for bearings of such dimensions as are used in practice when $EF = 2{\cdot}2\ E_1F_1$, and owing to the greater freedom with which the lubricant can escape at the end D and the sides near it, the point of maximum pressure p is somewhat nearer C than D. The curve at the top of the figure indicates, approximately, the pressure at different points of such a film, tending to force the surfaces apart. The direction in which the load acts, normal to AB, does not necessarily coincide with p, but with the centre of the area enclosed by the curve and base line of the pressure ordinates.

The pressure exerted by the film must always be equal to the resultant external force which, neglecting the obliquity of CD, is perpendicular to AB, and tends to force the surfaces together. When the surfaces are free to assume any position, the pressure of the film, inclination of surfaces, etc., adjust themselves to suit the load and its point of application, and the nearer the surfaces are caused to approach each other the greater is the friction and consequent pressure for the same velocity.

The relations obtaining between the load, pressure, etc., under these circumstances have been determined by Prof. Osborne Reynolds.

In the case of a surface CD of infinite width in a direction perpendicular to the paper he makes

$$h_0 = k\frac{\text{[illegible]}W}{\text{[illegible]}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and the force required to keep them in relative motion*

$$F = k\frac{\text{[illegible]}}{h_0} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\therefore \frac{\text{[illegible]}}{h_0^2} \propto \frac{\mu U W}{l} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and

$$F \propto \sqrt{\frac{\mu U W}{l}} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Lubrication of Cylindrical Surfaces.—The cylindrical is by far the most common form of bearing surface, and is the one with which most of the experiments recorded have been made. Until Mr. Tower's results were published little was really known concerning the effects produced by varying the method of applying the lubricant. He shewed that many of the methods in use were very imperfect, the oil holes and oil ways often cutting across those portions of the surfaces where the pressure of the film should be at its greatest, and allowing the lubricant to escape. With properly-shaped brasses resting upon well lubricated journals, he succeeded in obtaining results which Prof. Osborne Reynolds demonstrated were in accordance with hydrodynamical theory. The method of applying the lubricant, and the machine with which he experimented are described in another chapter.

A brass which has been running for some time upon a lubricated cylindrical journal wears in such a way that the radius is always slightly greater than that of the journal. When forced into contact, therefore, the brass and journal do not touch over the whole of their surfaces. On the other hand, when the journal is in rapid motion, and the weight on the brass is not too great, the surfaces are separated from each other by a continuous oil film. Fig. 30 shews a section through such a brass and journal, the latter rotating in the direction of the arrow, the surfaces being respectively AB and CD.

The curved surfaces AB and CD have their centres at I and J, a line drawn through which indicates the position of nearest approach E_1F. Between EF and E_1F the distance separating the surfaces decreases, the triangle E_1FG is consequently smaller than EFG, and during its passage the lubricant is compressed and tends to force the surfaces apart. As we go from E_1FG towards C the faces recede, and were it not for the flow of oil from the portion where the liquid undergoes compression, the pressure might be, and, indeed, sometimes does become, negative.

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* It must be clearly borne in mind that the load carried may be modified very largely by varying the direction in which it acts, for the inclination of the surfaces varies according to the distribution of the pressure, etc. Both in the case of inclined surfaces and parallel surfaces inertia effects, previously considered, must shew themselves. The wedging and the inertia actions, however, as will be seen from equations (15) and (16), have similar effects upon the relationships between the coefficient of friction, the speed, the load, and the viscosity; but the relationships between these values and the area and shape of the bearing do not appear to be *quite* similar. Still it is clear that, as is the case with contaminated and clean surfaces, the coefficient of friction of plane parallel surfaces is only slightly affected by variations in the area of the surfaces ni contact.

When there is no load the conditions are as shewn in fig. 31. Here the vertical pressures are shewn by the curved lines on the top of the figure. On the right-hand or 'on' side the pressure is positive, whilst on the left-hand or 'off' side it is negative, and the vertical components of these pressures balance each other. On the other hand, the horizontal component of the pressures to the left and right, indicated by the curves at the sides, will both act on the brass to the right, and as these will increase as the surfaces approach, the distance corresponding to JI (fig. 30) must be exactly such that these components balance the resultant friction.

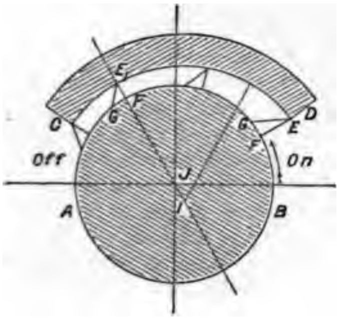

Fig. 30.

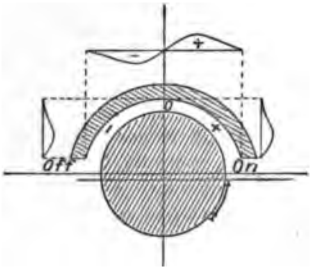

Fig. 31.

The thickness of the film at different points, and the variations of the position of E_1F with different loads, have been worked out mathematically by Prof. Osborne Reynolds, whose exact equations give results which agree very closely with the experimentally ascertained facts. For the full treatment of the subject the original papers should be consulted, as the results only can be given here.

Effects of Load and Speed.—In the case of plane surfaces, whether parallel or inclined, the frictional resistance is proportional to the square root of the load. In the case of cylindrical surfaces, however, the rubbing faces, owing to their curvature, cannot separate sufficiently, whilst still sustaining a load, to give this result, for when the load is increased E_1F decreases, the lubricant is prevented from escaping on all sides as freely as before, and EF, *i.e.*, the distance between the brass and journal on the on side, increases. Consequently, as the load is increased, the positive vertical component to the right increases (fig. 31) and overbalances the negative component to the left, which decreases, and E_1F, the point of nearest approach, moves to the left until the load reaches a particular value: above this load the point of nearest approach moves back towards O. During this change in the position of E_1F, the thickness of the film at different points alters in such a way that the viscous resistance which it offers to the motion of the journal remains nearly constant; and the friction is practically independent of the load when the speed is sufficient to maintain a pressure film between the two surfaces.

According to this reasoning the friction appears to be, *ceteris paribus*, approximately proportional to the area of the contact surfaces, the speed of the journal, and the viscosity of the lubricant, and is nearly independent of the load.

Before the journal commences to rotate, the lubricant being a viscous one, the load will have brought the brass into contact with the former at O; but at the ends it is separated by an appreciable space from the journal. At starting, and at very low speeds, the surfaces being in contact, there is friction of solid upon solid, the coefficient of friction is large, and the surfaces undergo some abrasion, but as the velocity of the journal increases, the surfaces gradually separate, more particularly if there be a plentiful supply of lubricant. This thickening of the film, as we have seen, can only take place to a limited extent owing to the curvature of the surfaces, so that with increasing speed the resistance becomes more nearly proportional to the speed and less affected by the load. At the outset, as with plane surfaces, when the oil film has scarcely established itself, the friction, *ceteris paribus*, varies with changes of load. However, owing to the curvature of the surfaces, the film very quickly reaches a maximum thickness.

TABLE X.—BATH OF OLIVE OIL. TEMPERATURE 90° F.
Journal, 4 in. wide × 6 in. long. Chord of Arc of contact = 3·92 in.

* NOMINAL LOAD. Lbs. per sq. in.	NOMINAL FRICTIONAL RESISTANCE PER SQ. IN. OF BEARING.							
	105 ft. per Min.	157 ft. per Min.	209 ft. per Min.	262 ft. per Min.	314 ft. per Min.	366 ft. per Min.	419 ft. per Min.	471 ft. per Min.
520	...	·416	·520	·624	·675	·728	·779	·883
468	...	·514	·607	·654	·701	·794	·841	·935
415	...	·498	·580	·622	·705	·787	·870	·995
363	...	·472	·580	·616	·689	·725	·798	·907
310	...	·464	·526	·588	·650	·680	·742	·835
258	·361	·438	·515	·592	·644	·669	·747	·798
205	·368	·430	·512	·572	·613	·675	·736	·818
153	·351	·458	·535	·611	·672	·718	·764	·871
100	·360	·450	·550	·630	·690	·770	·820	·890

* The nominal load per square inch is the total load divided by (4 × 6).

The above table gives the results obtained by Mr. Beauchamp Tower with *perfect*, *i.e.*, *bath* lubrication.

The loads range from 100 lbs. to 520 lbs. per square inch, nominal, and yet for each speed the frictional resistance is nearly a constant. Above speeds of 100 feet per minute low speed effects do not shew themselves, and the resistance will be seen to be nearly proportional to the square root of the speed instead of to the actual speed. Prof. Osborne Reynolds considers this as due to the fact that when the speed is increased the rate of shear which the film undergoes is likewise increased; the film becomes heated, its viscosity is decreased and less resistance to motion is encountered.

Prof. John Goodman has also published some results which he obtained with different speeds and different methods of lubrication, and which are given in the following table:—

TABLE XI.—RESISTANCE AT DIFFERENT SPEEDS.

Load, 300 lbs. Temperature, 40° C. Brass, ·5 in. × 4 in.

Oil-Bath.		Saturated Pad.		Oily Pad.	
Feet per Min.	Coefficient of Friction, μ_1.	Feet per Min.	Coefficient of Friction, μ_1.	Feet per Min.	Coefficient of Friction, μ_1.
2·6	·1610	4·70	·1610	5·2	·1540
7·8	·0630	7·80	·0910	**7·8**	**·0560**
11·0	·0140	**13·61**	**·0700**	11·0	·0021
15·7	**·0052**	38·20	·0021	17·3	·0021
57·1	·0017	88·50	·0024	27·2	·0028
67·0	·0017	111·50	·0028	61·3	·0042
103·7	·0021	122·00	·0035	88·5	·0070
122·0	·0028	149·70	·0063	122·0	·0091
146·6	·0035	183·20	·0098	161·0	·0126
164·9	·0038	213·60	·0126	183·0	·0168
183·2	·0042	...	...	209·4	·0217
...	...	...	...	242·9	·0252

At the speeds printed in heavy type in this table the friction is high, owing to the pressure film not having been properly formed. At higher speeds, however, as found by Osborne Reynolds, the friction is approximately proportional to the square root of the speed.

By means of a pressure gauge and of holes drilled in the brasses, Mr. Tower was able to measure the pressure of the oil film at various points of the surface.

Fig. 32 shews the exact curve of pressure calculated by Prof. Osborne Reynolds under conditions corresponding very closely with those in one of Mr. Tower's experiments in which, by means of a pressure gauge, he actually measured the pressure of the oil at several points in the film. The observed pressures as plotted by Mr. Tower are shewn in figs. 33 and 34. In this experiment, when the load was 100 lbs. per square inch, and the temperature was 70°, the thickness of the film at various points must, according to Prof. Osborne Reynolds, have been as follows:

Radius of brass – radius of journal = ·00077 ins.
E_1 F (Point of nearest approach) = ·000375 „
Angle O J F . . . = 48°.

The possible motion of the fluid in a direction perpendicular to that of the motion and parallel with the axis of the journal has not yet been referred to. In practice, the length of brasses is necessarily limited so that the oil can escape laterally. Such an escape will obviously prevent the pressure of the oil film from reaching its full height, except at considerable distances from the ends of the brass, and will cause it to fall to zero at the extreme ends.

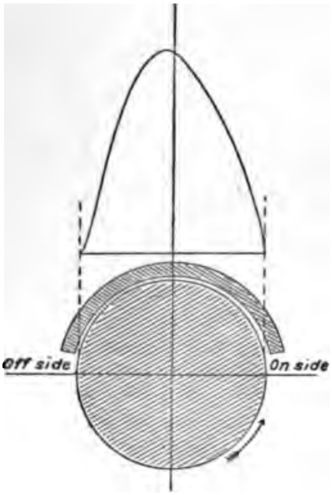

FIG. 32.

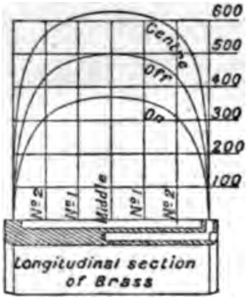

FIG. 33.

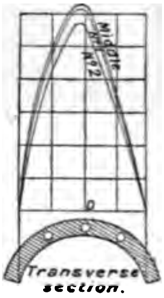

FIG. 34.

The lubricant does not, therefore, all flow in a direction parallel with the direction of motion, except at the centre, but follows paths curved from the centre of the brass, some reaching the sides when it escapes.

This is shewn by Mr. Tower, who measured the pressure at several points along the brass in a line through O, and found it follow the curves of pressure shewn in fig. 33, which correspond to those which might be expected to result from an escape of oil at the free ends.

Effects of Viscosity.—Just as, owing to the fact that the lubricating film can only thicken to an extent depending upon the difference

TABLE XII.—RESULTS OF MR. TOWER'S EXPERIMENTS.

Temperature Fahr.	Comp. Viscosities.	Coefficients of Friction for Speeds as below.							
		105 Feet per Min.	157 Feet per Min.	209 Feet per Min.	262 Feet per Min.	314 Feet per Min.	366 Feet per Min.	419 Feet per Min.	471 Feet per Min.
120°	35	·0024	·0029	·0035	·0040	·0044	·0047	·0051	·0054
110°	40	·0026	·0032	·0039	·0044	·0050	·0055	·0059	·0064
100°	48	·0029	·0037	·0045	·0051	·0058	·0065	·0071	·0077
90°	55	·0034	·0043	·0052	·0060	·0069	·0077	·0085	·0093
80°	65	·0040	·0052	·0063	·0073	·0083	·0093	·0102	·0112
70°	75	·0048	·0065	·0080	·0092	·0103	·0115	·0124	·0133
60°	89	·0059	·0084	·0103	·0119	·0130	·0140	·0148	·0156

between the radius of the brass and that of the journal, the frictional resistance is practically independent of the load, so the friction of a cylindrical journal should be proportional to the viscosity of the lubricant.

The effects of viscosity have been experimentally determined by Mr. Beauchamp Tower for various speeds above that at which the pressure film is fully formed. The lubricant used was lard oil, the viscosity of which was varied by heating the journal and brass. The viscosity of the lard oil used was not specified, but Prof. J. Goodman gives its probable comparative values at the temperatures stated.

Table XII. is taken from Mr. Tower's paper, with the addition of a column giving the comparative viscosities. The experimental results will be seen to be entirely in agreement with theory, the friction at each speed and temperature being as nearly proportional to the viscosity as can be expected when the experimental difficulties to be overcome are borne in mind. With increasing speed, however, the temperature of the oil film is raised more and more above that of the metallic surfaces, and the friction ceases to be proportional to the speed.

In the experiments on the pivot bearing it was pointed out that the slight disagreement between experiment and theory might be accounted for by the heating of the film. With parallel surfaces the friction varies only as the square root of the viscosity. No very marked effect was therefore to be anticipated from this heating, especially as the speeds were comparatively low. But in the case of a journal where the friction is proportional to the viscosity, the effect might be very marked. Indeed, there are grounds for believing that, as Prof. Osborne Reynolds contends, the reason why the resistance does not, in the case of a journal, increase at a rate proportional to the speed is that the rapid distortion which the oil suffers, heats it and lowers its viscosity.

Change of viscosity also has a considerable effect upon the carrying power. Table XIII., by Prof. J. Goodman, shews the effect which a change in the viscosity, brought about by rise of temperature, has upon the frictional resistance and carrying power of the journal, the speed being 7·8 feet per minute.

The actual viscosities at the temperatures of the experiments were not determined. They must, however, have been greatest at the lower temperatures, and *vice versa*. Although the speed is low, there is, on the whole, a reduction of the friction as the temperature increases, when the loads are small, but not so marked a change as might be expected. It will also be noticed that the greater the viscosity, the greater the load which the bearing will carry without undue friction resulting from the failure of the pressure film to form properly. In this table, the loads between which the coefficient of friction has a minimum value have been printed in heavy type.

The reduction in the frictional resistance which results from the lowering of the viscosity by the heating of the lubricating film is by no means advantageous, and accounts in a great measure for the failure of bearings to carry heavy loads at high speeds. The heating is most severe when the film is thinnest, *i.e.*, at the point E_1F, fig. 30. Reduced viscosity at this point greatly lowers the carrying power of the brass. Again, if from any cause the bearing should become warm, mineral oils become very fluid and cease to lubricate properly.

Effects of Area.—With parallel plane surfaces it was found that the friction does not increase much when the area is increased, for an increase of area brings about an increase in the *thickness* of the film. But here again a cylindrical form of bearing gives a different result, the frictional resistance being more nearly proportional to the area owing to the fact that when the speed is moderately high the film has a fairly constant effective thickness under all loads.

TABLE XIII.—OIL-BATH LUBRICATION.

Speed, 7·8 feet per minute.

Temperature 40°.			30°.		20°.	
Load.	μ_1.	F.	μ_1.	F.	μ_1.	F.
50	·0061	·30	·0080	·40	·0084	·42
100	·0038	·38	·0041	·41	·0042	·42
150	·0027	·40	·0028	·42	·0028	·42
200	·0020	·40	·0021	·42	·0021	·42
250	**·0016**	**·40**	·0021	·52	·0019	·47
300	·0017	·51	·0017	·51	·0016	·48
350	·0021	1·22	**·0015**	**·52**	·0014	·49
400	·0029	1·16	·0016	·64	**·0013**	**·52**
450	·0042	1·89	·0019	·85	·0013	·58
500	·0189	9·45	·0044	2·20	·0029	1·45
550	·0515	28·33	·0126	6·93	·0764	42·03
560	·0562	31·48	·0142	7·95	·0937	52·47
580	·0724	42 00	·0253	14·68	·1086	63·00

Table XIV., giving the results of some experiments by Prof. J. Goodman, brings this out very clearly. The frictional resistance at different loads does not vary very much. On the other hand, the long, narrow brass offers a very much smaller resistance to the motion of the journal than does the brass having a chord of contact measuring 2 inches. The area of the surfaces is in all cases proportional to the length of the arc of contact which is given for each size of brass. If the film were of even thickness throughout the length of the arc the friction would be simply proportional to its length. The film, however, is much thicker on the 'on' side where the lubricant enters than it is nearer the centre of the brass. The resistances offered to

TABLE XIV.—BATH LUBRICATION.

LENGTH OF BRASS, 4 INS. SPEED, 121·9 FEET PER MIN.

Width of Cord in contact 2 In. Angle subtended 180°.			1·75 122°.		1·5. 97°.		1·0 60°.		·5 29°.	
Total Load.	μ_1.	F.	μ_1.	F.	μ_1.	F.	μ_1.	F.	μ_1.	F.
50	·0441	2·20	·0458	2·29	·0418	2·09	·0210	1·05	·0126	·83
100	·0288	2·88	·0238	2·38	·0209	2·09	·0105	1·05	·0084	·84
150	·0192	2·88	·0160	2·40	·0140	2·10	·0070	1·05	·0056	·84
200	·0159	3·18	·0121	2·42	·0106	2·12	·0055	1·10	·0042	·84
250	·0128	3·20	·0097	2·42	·0085	2·12	·0044	1·10	·0034	·84
300	·0103	3·09	·0081	2·43	·0071	2·13	·0037	1·11	·0028	·84
350	·0085	2·97	·0070	2·45	·0061	2·13	·0033	1·15	·0024	·84
400	·0071	2·84	·0062	2·48	·0054	2·16	·0029	1·16	·0021	·84
450	·0062	2·79	·0055	2·47	·0049	2·20	·0028	1·26	·0019	·84
500	·0058	2·90	·0049	2·45	·0044	2·20	·0029	1·45	·0017	·84
550	·0051	2·85	·0045	2·47	·0040	2·20	·0027	1·48	·0015	·84
Mean	...	2·89	...	2·42	...	2·14	...	1·18	...	·82

the motion of the journal by those portions of the brass near the 'on' and 'off' sides are, therefore, less than near the middle of the bearing, and as the brass is cut away at the sides, the thickness of the film is also very slightly reduced. The reduction of the resistance is, therefore, not quite proportional to the reduction of the area, as will be seen by comparing the lengths of the arcs with the mean frictional resistances. A closer approximation of the results obtained with theory cannot be expected, as everything depends upon the curvature of the surfaces remaining unaltered during the experiments.

Alternating Pressures.—In some cases the loads upon bearings are by no means constant, for the faces often alternately approach and recede from each other. When this is the case, and the alternation is very rapid, the bearing will carry a very great weight, for at each alternation the pressure is completely relieved and the oil 'trapped' cannot be expelled during the short time the load rests on the bearing. The large ends of connecting rods may be instanced as cases in point. Here, although the pin is rapidly rotating in the brasses, the load frequently reaches several tons per square inch. On the small end brasses the load may be even greater, for the angular movement of the brass on the pin is only small. The reason the lubricant cannot escape whilst the pressure lasts is doubtless that the volume of oil which can be 'squeezed' out by any particular load is proportional to the cube of the thickness of the film.

Wear of Cylindrical Bearing Brasses.—To obtain a low coefficient of friction when the bearing surfaces are cylindrical in form, the radius of the journal must be rather smaller than that of the brass, so as to leave space for a film of the lubricant to insinuate itself between the surfaces. When the bearings have been newly and accurately fitted together, the friction is generally high, but after they have been at work for some time the resistance is found to have largely decreased. This results mainly from the altered shape of the brasses consequent on wear. The exact nature of the wear which takes place in rubbing surfaces is, therefore, of the utmost importance, for upon it depends very largely the frictional resistance of the bearing. Unfortunately this aspect of the question has only received a very small amount of attention. Indeed, until more evidence is forthcoming concerning the results of wear, we have no guarantee that the friction is really independent of the load; for there is every reason to believe that upon the load largely depends the shape the surfaces assume from wear. Thus, although when the surfaces have arrived at a certain shape rapid changes of load do not alter the frictional resistance, it is not unlikely that for each load, if it act for any length of time, there is a different curve of brass, and therefore a different frictional resistance.

As at high speeds the oil film is practically continuous and keeps the surfaces quite apart, such wear as then occurs must result from the intrusion of solid particles rather larger in diameter than the thickness of the lubricating film. But doubtless the chief wear takes place at low speeds when the surfaces are in contact. Actual abrasion then occurs.

When moving very slowly, the brass actually touches the journal at E_1F (fig. 30), or even on the 'on' side of O (fig. 31), but at ordinary speeds the liquid is *wedged* between the surfaces and keeps them apart on this side. Thus the wear is almost wholly on the 'off' side, where, except at considerable speeds, the surfaces touch, and the brasses when not very narrow are worn to a larger radius than that of the journal. When the journal is not in motion, the point of contact will be at O, consequently as the speed changes, the position of abrasion will also change. The action is the same whether the brass be lubricated by a siphon supplying oil to the crown of the bearing, or by a pad beneath the journal. However, when the chord of the arc covered by the brass is small, the wear tends to become more evenly distributed over the whole bearing surface. Even then the wear tends to make the radius of the brass larger than that of the journal, and thus renders efficient lubrication possible.

In the case of railway journals and brasses, the wear is sometimes on one side of the brass and sometimes on the other, according as the direction of motion of the vehicle changes; but when the shaft or journal always rotates in the same direction, the wear is always on the same side. This one-sided wear often disturbs the adjustment of mechanical oil-testing machines, and effects arising from this cause should always be looked for.

Imperfect Lubrication.—Until quite recently, full advantage was seldom taken of the viscous lubricating properties possessed by lubricants. This arose from many causes. Sometimes it is difficult to apply the lubricating fluid in the most effective manner, whilst in many cases the more perfect the system from a friction point of view, the greater the waste of oil.

TABLE XV.—INFLUENCE OF METHOD OF LUBRICATION AND CONTACT AREA UPON FRICTIONAL RESISTANCE.

Length of Bearing, 4 Inches; Speed, 122 Feet per Min.

Method of Lubrication.	Width in Inches of Chord of Bearing Surface.				
	2·0	1·75	1·5	1·0	0·5
	Frictional Resistance in Lbs.				
Oil Bath, . . .	2·89	2·42	2·14	1·18	0·82
Saturated Pad, . .	4·47	3·98	2·49	2·10	1·06
Oily Pad, . . .	7·97	6·62	5·80	3·80	2·70

Bath or 'perfect' lubrication is obtained by allowing the under side of the journal to dip into a bath of the lubricant. In this way the journal picks up and throws against the brass a thick film of oil, and the result is 'perfect lubrication,' *i.e.*, the thickest film is secured which the bearing can automatically maintain.

Pad lubrication is obtained by pressing a woollen or felt pad soaked with the lubricant against the journal. When the pad rests in a bath of the lubricant and is kept thoroughly soaked, the results obtained are not greatly inferior to those given by the bath. When, however, the supply of oil to the pad is deficient, the difference is marked, as will be seen from Table XV., by Goodman.

Ball and Roller Bearings.—Of late years ball and roller bearings have come into very extensive use, having been found very suitable for slow stopping trains, motor-cars, cycles, dynamos, and other machines the bearings of which have to carry moderate loads.

TABLE XVI.—RUDGE BALL BEARING. WHITE 'NEUTRAL' OIL.

Load in Lbs.	Speed, 19 Revolutions per Minute.		Speed, 157 Revolutions per Minute.		Speed, 350 Revolutions per Minute.	
	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance, Lbs.
10	·0060	·06	·0105	·10	·0105	·10
20	·0045	·09	·0067	·13	·0120	·24
30	·0050	·15	·0050	·15	·0110	·33
40	·0052	·21	·0052	·21	·0097	·39
50	·0054	·27	·0054	·27	·0090	·45
60	·0050	·30	·0055	·33	·0075	·45
70	·0049	·34	·0054	·38	·0068	·47
80	·0048	·38	·0062	·49	·0060	·48
90	·0050	·45	·0068	·61	·0060	·54
100	·0058	·58	·0069	·69	·0057	·57
110	·0054	·59	·0065	·71	·0060	·66
120	·0055	·66	·0075	·90	·0057	·68
130	·0058	·75	·0078	1·01	·0062	·81
140	·0056	·78	·0077	1·08	·0060	·84
150	·0060	·90	·0083	1·24	·0062	·93
160	·0075	1·20	·0081	1·29	·0058	·93
170	·0079	1·34	·0078	1·33	·0055	·93
180	·0079	1 42	·0078	1·40	·0053	·95
190	·0087	1·65	·0076	1·44	·0054	1·03
200	·0090	1·80	·0081	1·62	·0060	1·20
Means	·0060	...	·0070	...	·0071	...

One of the early forms of ball-bearing known as the 'Rudge' was experimented upon by Prof. J. Goodman. The results of his experiments are given in Tables XVI. and XVII. The results with the white 'neutral' oil are rather irregular, but their average clearly shews that, as with the pale American oil, the coefficient of friction varies very little with moderate loads; the frictional resistance, therefore, varies almost directly as the load.

To ascertain the effects of viscosity, the bearing was heated by a Bunsen gas-burner from 20° to 60° C., but no difference could be detected in the friction. The experiment was repeated with different lubricants, loads, and velocities, with the same negative results. In the case of ball bearings a lubricant only alters the area in contact over which slip takes place, and although it does not decrease the friction it prevents undue wear, and prolongs the life of the bearing.

TABLE XVII.—RUDGE BALL BEARING. PALE AMERICAN OIL.

Load, Lbs.	Speed, 19 Revolutions per Minute.		Speed, 157 Revolutions per Minute.	
	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance, Lbs.
10	·0075	·07	·0060	·06
20	·0075	·15	·0075	·15
40	·0071	·28	·0075	·30
68	·0070	·42	·0075	·45
80	·0071	·57	·0071	·57
100	·0073	·73	·0072	·72
120	·0071	·85	·0069	·83
140	·0072	1·01	·0067	·94
160	·0072	1·15	·0066	1·06
180	·0072	1·30	·0066	1·19
200	·0073	1·46	·0066	1·32
Means	·0072	...	·0068	...

From these experiments the following laws, therefore, are deducible:—

1. The coefficient of friction is nearly constant for all ordinary loads; hence, unlike lubricated cylindrical bearings, the frictional resistance varies directly as the load.
2. The friction is unaffected by change of temperature, and therefore by moderate changes in the viscosity of the lubricant.

The coefficient of friction of ball bearings at high speeds is rather higher than that of ordinary bearings when bath or saturated pad tion is used, but is less than the friction of ordinary brasses the latter are lubricated by less perfect methods. The friction and roller bearings is also small at very low speeds and with loads, much smaller indeed than could be obtained with ordinary gs at such speeds even by bath lubrication.

ing to their small frictional resistance roller bearings have lately ried and have given very favourable results on electric railways, and motor-cars.

Bailey Marshall* states that on railway vehicles the starting is, in many cases, as low as 3 lbs. per ton, a figure which com- favourably with the frictional resistances of ordinary bearings h speeds when well lubricated; but it seems doubtful whether bearings will, when used for such high speeds, give better than brasses of the ordinary design.

the case of ball bearings the design should be such that the nt used can escape readily on each side of the balls as they roll ir races; with rollers, however, the lubricant must be pushed in front of them. On this account the viscosity of the lubricant ust have an appreciable effect upon the friction in the latter case.

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* *Roller Bearings* (pamphlet), London, 1897.

CHAPTER V.

LUBRICANTS.

THEIR SOURCES, PREPARATION, AND CHIEF PROPERTIES.

LUBRICANTS are, with few exceptions, fluid or semi-fluid substances, capable of forming and maintaining between friction surfaces films of sufficient thickness to keep the surfaces apart, thus abolishing the solid friction and substituting for it the much less considerable friction of the fluid itself. The substances which possess in the highest degree the necessary properties belong to the class of bodies known as fixed oils and fats. Until the latter half of the present century lubricating oils were almost exclusively derived from the animal and vegetable kingdoms, though cart-grease had been prepared from petroleum in Galicia from a very early period (*Redwood*), while early in the present century the advantages of petroleum as a lubricant free from 'gumming' properties were sufficiently well known to lead to its more general use in places where it could be obtained. The rise and development of the modern petroleum and shale oil industries, stimulated by the increased demand for lubricants due to the introduction of railways and the extended use of machinery, has led to the production of immense quantities of lubricating oils, which, besides largely augmenting the general supply, have, owing to their cheapness and other advantages, displaced to a great extent the older lubricants. We shall, therefore, commence with a description of this class of oils, which, being derived from mineral sources, have received the name of

A.—MINERAL OILS.

I. Sources.

(*a*) **Petroleum.**—Crude petroleum is a highly complex liquid product which is found very abundantly in various parts of the world, either issuing naturally from the ground or reached by boring. Its urrence is not limited to any particular country, continent, or logical formation, but by far the greater volume is obtained in e United States of America and in the neighbourhood of Baku in ucasia (Russia). The total annual production of crude petroleum as been estimated to amount to over 5000 millions of gallons, disibuted as follows *:—

	Millions of Gallons.
United States,	2500
Russia,	2250
Austria,	87
Sumatra,	72
Java,	30
Canada,	29
Roumania,	24
India, Japan, Germany, Peru, Italy,	34
	5026

The great bulk of this crude petroleum, after refining, is *illuminating oil*, and only a small proportion is *lubricating oil*. Thus, of the manufactured petroleum exported from the United States in 1895 and 1896, 92 per cent. was illuminating oil, and only about 6 per cent. lubricating oil; this latter proportion, though relatively small, amounted nevertheless to nearly 43½ millions of gallons, of which the United Kingdom took about half.† Were there a greater demand, the production of lubricating oil could be immensely increased, especially from Russian petroleum.

Crude *American* petroleum is obtained chiefly in Pennsylvania, Ohio, and West Virginia. It varies very much in character in different districts, ranging in colour from pale amber to dark greenish- or brownish-black, and in specific gravity from about 0·78 to 0·94 (*Höfer*). Some oils are highly limpid, and are composed for the most part of the lighter hydrocarbons suitable for burning in lamps; others, like the heavy oil of the Bradford and Franklin districts of Pennsylvania, contain a large proportion of lubricating hydrocarbons. A few crude oils can be used for lubricating almost without treatment (see "Natural Oils"). Most of the crude petroleum obtained in the United States is distilled for illuminating oil and naphtha, only the still residues ('residuum') being worked up into lubricating oils and paraffin wax; but there are some heavy oils, such as those of the Franklin and Smith's Ferry districts of Pennsylvania; of Mecca, Ohio; of Volcano, West Virginia; and the recently discovered oil at Scur Lake, Texas,‡ which, being chiefly valuable for the manufacture of lubricating oil, are treated separately. Researches too numerous to mention have shewn that American petroleum is composed mainly of hydrocarbons of the paraffin series, C_nH_{2n+2}, with smaller quantities of naphthenes, and of benzene and its derivatives. Traces of sulphur are met with in most petroleum, also oxygenated bodies of acid and phenolic character, and variable traces of mineral matter.

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* Washington Despatch. See *Chem. Trade Jour.*, July 1, 1899.

† *Jour. Soc. Chem. Ind.*, 1896, p. 687; and 1897, p. 271.

‡ *Jour. Soc. Chem. Ind.*, 1898, p. 287.

Crude *Caucasian* petroleum is, in many respects, specially interesting; in the antiquity of historical references to it; in the comparatively small area within which the supply is obtained; in the extraordinary productiveness of the wells and in the peculiar character of the hydrocarbons of which the oil is mainly composed. According to the researches of Markownikoff and Ogloblin, and others, at least 80 per cent. of crude Baku petroleum consists of hydrocarbons of the naphthene series, C_nH_{2n}, isomeric with the olefines, but differing from them in not combining directly with bromine. Naphthenes are closed-chain hydrocarbons, also known as polymethylenes, one of the most important being hexamethylene or hexhydrobenzene, C_6H_{12}, which has been obtained in large quantity from Russian and in small quantity from American petroleum.[*] Russian petroleum also contains paraffins and a considerable quantity of aromatic hydrocarbons.

Caucasian petroleum is more uniform in composition than the American product. It usually ranges in specific gravity from 0·850 to 0·875; yields a larger proportion of lubricating oil, less illuminating oil and less naphtha than American petroleum, but no paraffin wax. Owing to the almost entire absence of solid hydrocarbons, Russian lubricating oils will bear exposure to a much lower temperature than American oils without solidifying.

Galician petroleum is stated by Redwood to have been collected in a primitive fashion and used as a cart-grease from very early times. The Galician oil-fields are very extensive, and produce oils of very varied character, both light and heavy. The modern industry ranks next in importance to that of Russia, though far below it in point of bulk. Crude Galician petroleum is composed chiefly of hydrocarbons of the paraffin series. According to Dr. Young it contains more naphthenes and aromatic hydrocarbons than American, but probably less than Russian petroleum. It yields 55 to 65 per cent. of lamp oil and from 30 to 40 per cent. of residuum from which lubricating oils are obtained.[†]

Canadian petroleum resembles the oil of Lima (Ohio) in having an offensive odour and containing a notable proportion of sulphur. The production is comparatively small, and the oil is chiefly refined for home consumption.

Among the minor sources of mineral lubricating oil may be mentioned the heavy petroleums of *Roumania*, *Hanover*, and *Alsace*, nd the Rangoon oil or tar of *Upper Burma*. *Alsace* petroleum s rich in lubricating oil, and yields from 55 to 60 per cent. of residuum.

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[*] Young, *Jour. Chem. Soc.*, 1898, Transactions, p. 905.

[†] For an interesting and very complete account of the Galician petroleum and ozokerit industries, see a paper by Redwood, *Jour. Soc. Chem. Ind.*, 1892, pp. 93-119.

(*b*) **Shale.**—Although by far the greater proportion of the lubricating oil of commerce is now obtained from petroleum, it is of interest to remember that shale oils were the first to be produced on a large scale even in America. Prior to the boring of Drake's well in 1859, which was the commencement of the United States petroleum industry, a number of works were established in that country for the production of oil from coal and shale, and Boghead cannel was even imported from Scotland for the purpose; these factories, which worked under licence from Dr. James Young, the founder of the Scottish Shale Oil Industry, were subsequently converted into petroleum refineries (*Redwood*). Young's first patent for obtaining paraffin oil from bituminous coal was taken out in 1850, and the mineral which he used was Boghead cannel, a rich bituminous mineral yielding by distillation from 120 to 130 gallons of oil per ton. The supply of this mineral soon became exhausted, and since then the Scotch oil has been produced from the bituminous shales of the coal measures. The manufacture of paraffin oil from shale at the works of the Broxburn Oil Company has been described by D. R. Steuart (*Jour. Soc. Chem. Ind.*, 1889, pp. 100–109). The shale is a dark grey or black mineral with a laminated or horny fracture. The greater proportion (73 to 80 per cent.) consists of *mineral matter*; the remainder (27 to 20 per cent.) is *bitumen*, composed chiefly of carbon and hydrogen with some nitrogen and sulphur. When the shale is heated to a very low red heat in retorts, this bitumen undergoes *destructive distillation*, splitting up into water, ammonia, gas, and oil. Each ton of shale distilled at Broxburn yields on an average 30 gallons of crude oil, 65 gallons of ammoniacal water, and nearly 2000 cubic feet of permanent gas, which is used for lighting the works and for fuel.

(*c*) **Crude Shale Oil** is dark green in colour, has a specific gravity of 0·860 to 0·890, and is semi-solid at ordinary temperatures owing to the large quantity of solid paraffins ('paraffin wax') contained in it. When warmed to 90° or 100° F., the oil becomes quite fluid. Chemically, it is composed chiefly of hydrocarbons of the paraffin and olefine series, the latter predominating in the fractions used as lubricating oil. Naphthenes and aromatic hydrocarbons are also present in large quantity (Heusler, *Jour. Chem. Soc.*, 1898, Abstracts I. 101).

II. Manufacture.

The manufacture of lubricating oils from crude petroleum and shale oil is a branch of a very extensive industry. The great variety of hydrocarbons of which the crude oils are composed affords material for the manufacture of numerous products. The lightest and most volatile hydrocarbons compose **Crude Naphtha**, from which rhigolene, gasoline, benzoline, and similar products are obtained. These liquids, which are devoid of all lubricating property, form highly volatile and inflammable 'spirits,' used for freezing, making air gas, carburetting coal gas, and for solvent and other purposes. Hydrocarbons of higher boiling-point and specific gravity, which are still too fluid and volatile to be used for lubricating, compose the **Illuminating Oils** of commerce known as kerosene, petroleum, paraffin oil, etc. The heaviest and least volatile hydrocarbons are alone used for the manufacture of **Lubricating Oils**, **Paraffin Wax**, and **Vaseline**. The refiner's business is to separate the various products from the crude oil and purify them for use, and this he does by distillation and chemical treatment.

The value of distillation depends upon the fact that the different constituents of the crude oil boil and volatilise at different temperatures, the naphtha coming over first, then the illuminating oils, then some 'intermediate' oils used for gas making, or destructively distilled so as to increase the quantity of illuminating oil (see below), leaving the heaviest hydrocarbons, unless the distillation is continued to dryness, as a residue or **Residuum** in the still. By separate fractional distillation, the naphtha is subsequently split up into gasoline, benzoline, etc., the crude illuminating oil into products of different specific gravities and flashing-points, and the residuum into lubricating oils of various grades and paraffin wax.

In practice, however, the distillation, especially of the heavier fractions, is never a simple process of separation, as is proved by the fact that products are found in the distillates, which do not exist in the original liquid. During the distillation the heavier hydrocarbon vapours partly condense on the upper and cooler part of the still and fall back into the boiling liquid, while, in distilling the heavy oil, the boiling has to be very vigorous to keep up the stream of vapour issuing from the retort, which necessitates a strong fire and a high temperature at the bottom and sides of the retort.* The prolonged and excessive heating to which the heavier hydrocarbons are thus subjected gradually splits them up, partly into permanent gases (marsh gas and hydrogen), partly into liquid hydrocarbons of lower boiling-point and viscosity which distil over, and partly into tarry products which remain in the still. It has been found, in fact, that by setting the still so that the upper part is kept cool, and conducting the distillation slowly in order to promote condensation, or by distilling under increased pressure and so raising the boiling temperature of the liquid, the **destructive distillation** or '**cracking**' of the heavier hydrocarbons may be promoted to such an extent as to largely increase the natural yield of illuminating oil at the expense of the heavier fractions. Large quantities of crude petroleum, in which the residuum is not of special value for the preparation of lubricants, are distilled in this way in the United States, the illuminating distillate being increased from a normal proportion of about 50 per cent. to as much as 70 or 75 per cent., and the residuum reduced to as little as 6 per cent. According to Steuart, the hydrocarbons of petroleum are more readily split up than those of shale oil, and in Scotland cracking for the production of illuminating oil is not practised. A certain amount of destructive distillation is, however, necessary for the production of the paraffin wax which is such an important product of the shale oil industry. The quantity of crystalline wax obtainable from crude shale oil by direct freezing is much less than is obtained by freezing the distillates obtained by distilling the oil in such a way as to cause partially destructive changes.

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* Steuart (*Jour. Soc. Chem. Ind.*, viii. 106) has pointed out that whilst water in being converted into steam increases in volume 1700 times, burning oil increases less than 200 times, and heavy oil less than 100 times. In distilling the heavy oil a great deal has therefore to be converted into vapour before enough is formed to reach the point of exit from the still, and as the specific heat of the vapour is low, it is easily condensed and falls back into the boiling liquid.

Destructive distillation which is so valuable in increasing the yield of illuminating oil and in the production of paraffin wax has been found to be most detrimental to the quality of the lubricating oil, reducing the viscosity, lowering the boiling- and flashing-points, and tending generally to the production of an inferior product. When, therefore, the primary object of the distillation is to obtain the lubricating oil with its viscosity, chemical stability, and other valuable qualities unimpaired, every care is taken to reduce the amount of *destructive* distillation to a minimum. With this object the **Steam Refining Process** was introduced about 1870. In this process, which is largely used in the manufacture of lubricating oils from crude petroleum and petroleum residuum, a current of steam superheated to the required temperature (varying from 150° to 300° C.) is blown through the oil during the distillation, by which means the hydrocarbon vapours, instead of remaining in the still and undergoing decomposition, are swept rapidly forward into the condensing worm. Further improvements have been effected, especially in the distillation of the heavier hydrocarbons, such as form vaseline and cylinder oils, by conducting the distillation in a partial **vacuum**, maintained by means of an exhaust ejector or other appliance connected to the end of the condensing worm. The boiling temperatures of the hydrocarbons are thus lowered, and the rapidity of the distillation is much increased.

In addition to these modifications in the process of distillation, the plant has also been improved. The thick-walled cast-iron stills at first employed, in which the proper regulation of the temperature was impossible, have given place to stills of wrought-iron or steel; the vertical form of still has been abandoned in favour of the horizontal, so as to increase the evaporating surface, and the stills are provided with low domes or short goose-necks in order to still further diminish the distance traversed by the heated vapours. The result of all these improvements in the plant and processes has been a great improvement in the quality of mineral lubricating oils, to which must be attributed the rapid manner in which their use has extended during recent years.

The lubricating oils manufactured from crude petroleum in the United States are of three kinds, viz.:—*natural*, *reduced*, and *distilled* oils.

(*a*) **Natural Oils.**—A limited quantity of crude petroleum is found in the United States in which the proportion of lubricating hydrocarbons is so large that the crude oil only needs purification from suspended and tarry impurities by settling, straining, or filtering through charcoal in order to render it fit for use. Lubricating oils obtained in this way are known as 'natural oils,' but very little oil of this description is now produced.

(*b*) **Reduced Oils.**—Crude petroleum rich in lubricating oil, but too fluid for use as a lubricant without treatment, is carefully distilled with steam or *in vacuo*, so as to avoid cracking, until the lighter hydrocarbons have been driven off. The distillation is then stopped, and the dark-coloured oil remaining in the still, reduced in volume but increased in viscosity, is known as 'reduced oil.' Such oils have considerable lubricating value, and are largely used on railways and for heavy machinery. The chief objection to them is the tarry matter which they contain, which stains the machinery and paint, and interferes with the free siphoning of the oil. In the manufacture of *cylinder oil*, suitable descriptions of petroleum are carefully reduced at as low a temperature as possible, *in vacuo*, and for *filtered cylinder oil* the highly viscous residues thus obtained are repeatedly filtered through animal charcoal kept sufficiently warm to maintain the oil fluid, until the required degree of transparency is obtained. The reducing process is not always carried out in stills; the lighter hydrocarbons are sometimes evaporated by exposing the oil to the rays of the sun in shallow tanks containing water warmed by steam coils, the oil floating on and depositing its suspended impurities in the water. This process is known as 'sunning,' and the product as 'sunned oil.'*

(*c*) **Distilled Oils.**—These oils are obtained from residuum. Those produced from American petroleum contain paraffin wax, and are known as '*paraffin oils*.' The Russian oils contain little or no paraffin. Distilled oils usually undergo treatment with acid and alkali by which they are partially decolorized and made transparent; in this way the '*pale oils*' are produced.

Residuum, as already described, is the tarry residue remaining in the crude-oil stills after the naphtha and illuminating oils have been distilled over with more or less cracking. As a rule the distillation of the crude oil is stopped at this stage, the residuum is withdrawn from the still and, after standing for some time to allow the fine particles of coke contained in it to settle out, is transferred to special stills called 'tar-stills,' in which the distillation for lubricating oils is conducted with superheated steam, or *in vacuo*, generally in separate factories devoted to the manufacture of lubricating oil. The residuum obtained in the United States is very different, both in quantity and in quality, from the Russian product. By cracking, the yield of residuum from Pennsylvanian petroleum is reduced to as little as 5 to 10 per cent., whilst from the crude oil distilled at Baku as much as 36 to 60 per cent. of residuum is obtained. This difference in the yield is not entirely due to the different character of the crude oil. Crude Pennsylvanian oil distilled without cracking will give from 20 to 30 per cent. of lubricating oil, and correspondingly less illuminating oil. At Baku, the residuum called by the Russians '*astatki*,' and by the Tartars '*mazut*,' is in great demand for fuel, and there is not the same inducement to reduce the yield by cracking as in the United States.

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* A sunning process is also used in the manufacture of 'bloomless' oil (see p. 94).

American residuum contains a variable proportion of solid hydrocarbons, and varies accordingly both in consistency and in specific gravity; it is the source of all the paraffin wax obtained in the United States. On the other hand, the Russian astatki produced at Baku is a more fluid oil having a uniform specific gravity of 0·90 to 0·91, and containing so little solid hydrocarbons as to yield practically no paraffin wax.* Lubricating oil of a kind has been made in the United States by simply filtering the residuum through steam-heated filters, but the unstable character of the product and the accompanying tarry matters unfit it for any but the roughest purposes. Russian residuum is similarly employed, after separation of water and treatment with sulphuric acid. But the usual method is to refine the oil by distillation with superheated steam. In the United States the distillation is carried to dryness. The first 20 to 25 per cent. of the distillate is a very fluid oil of about 0·834 sp. gr., which is either returned to the crude oil tank or is refined as a special high flash-point burning oil. The oil that follows is lubricating oil and contains the paraffin wax; it is either collected all together or in separate fractions. Just at the end of the process, when the bottom of the still is red-hot, a thick resinous product of light yellow colour and nearly solid consistency distils over, which is used as a lubricant for the necks of rolls,† or, according to Sadtler, is added to paraffin oils to increase the density and lower the cold-test. About 12 per cent. of coke remains in the retort, which is used for the manufacture of electric light carbons. The paraffin oil, if collected all together, is washed first with acid and then with alkali and is then reduced in temperature by ammonia freezing machines, which causes the paraffin to crystallize. The semi-solid mass is subjected to hydraulic pressure between bagging, and the solid crystalline cake which remains is converted into refined paraffin wax. The fluid oil which drains from the press is carefully redistilled and collected in separate fractions, yielding a variety of lubricating oils ranging in density and viscosity from the lightest and thinnest spindle oil to heavy machine oil and even cylinder oil, though cylinder oils are not usually made from residuum. If the paraffin oil, instead of being collected all together, is fractionated at the first distillation, then those fractions which contain the wax are separately treated for its recovery. Thus, according to Redwood, the second fraction following the oil of 0·834 sp. gr. (see above) may be collected so as to have a sp. gr. of 0·860–0·870, and may amount to 25 per cent. of the original residuum. This fraction may be subdivided by redistillation, or may be made into '*Neutral*' or '*Bloomless*' oil by cooling to separate the paraffin, filtering through bone-black to remove colour and odour, and exposing to the sun and air in shallow tanks or treating with nitric acid or nitro-naphthalene, or in other ways to remove fluorescence or 'bloom.' 'Neutral oil' has a very low viscosity, and is largely used for the adulteration of animal and vegetable oils, for which reason it is debloomed so as to remove the fluorescence which would betray its presence. The distillate following the neutral oil is the 'stock' for engine oil, and the percentage is determined (with a corresponding inverse variation in the proportion of the second fraction) by the use to which the product is to be put. For heavy machine oil the proportion is reduced, so that a distillate of sp. gr. 0·928 to 0·933 may be obtained, and after the paraffin has been separated the viscosity is sometimes still further increased by distilling off some of the more volatile constituents by means of superheated steam and filtering the 'reduced' oil through charcoal.

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* Engler, *Jour. Soc. Chem. Ind.*, 1886, p. 477.

† *Jour. Soc. Chem. Ind.*, 1882, p. 142.

Previous to the chemical treatment of the lubricating oil distillates, they are freed from mechanically mixed water by settling, and the last traces of moisture are got rid of by heating the oil in tanks fitted with steam coils. The dried oil is then thoroughly agitated with concentrated sulphuric acid, the proportion of acid varying from 4 to 12 per cent., according to the strength of the acid and the amount of impurity in the oil. After thorough settling, the clear oil is drawn off, agitated with a solution of caustic soda, and again allowed to settle; it is then well washed with warm water, allowed to rest until clear, and finally dried by being heated in shallow pans provided with steam coils until the oil is bright. Sometimes the oil after being treated with acid is pumped into a still containing a solution of caustic soda amounting to from 2 to 4 per cent. of the oil, and is redistilled from the soda, by which process free acid and sulphonates are more perfectly removed and the oil is improved in colour. The treatment with sulphuric acid removes tarry matters, as well as some of the more easily acted on hydrocarbons,* and the soda neutralizes the remaining traces of sulphuric acid as well as organic acids contained in the oil or resulting from treatment. The chemical changes which take place are by no means fully understood. Secondary reactions occur, certain of the hydrocarbons being very liable to undergo oxidation with formation of acid products, especially during the alkaline treatment. Great care and attention are therefore needed to produce the most highly refined oil, which is clear and bright, contains neither acid nor alkali, and does not become turbid on standing.

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* It is said that some valuable lubricating hydrocarbons are withdrawn by the action of sulphuric acid.

(*d*) **Russian Oils.**—The manufacture of lubricating oils from astatki was commenced by V. I. Ragosine in 1876, and two years later the Russian oils were first introduced into England.* Up to that time naphtha and illuminating oil were the only products manufactured from the crude Caucasian petroleum, and the astatki was either burned as fuel or entirely wasted. Even now the greater proportion is used as fuel, and only a comparatively small proportion, about 10 per cent. according to Redwood, is manufactured into lubricating oils; but, considering the enormous quantity of astatki produced, even this small proportion amounts to a considerable volume.

The astatki,† which is stored in large tanks sunk in the ground,‡ is first pumped into raised tanks in which it is heated by steam coils to facilitate the settling of water and other impurities likely to cause frothing and explosive ebullition. The clarified oil flows by gravitation into the stills, which are horizontal wrought-iron vessels of circular or elliptical section, waste oil being the fuel used for heating them. When the temperature has risen to 130° or 140° C. (266°–284° F.) a fairly regular ebullition sets in, and distillation commences at about 150°–160° C. (302°–320° F.). Superheated steam is then admitted through perforated pipes placed very near the bottom of the retort, and the distillate is collected in separate fractions as the temperature rises, until the oil coming over has a density of 0·915 to 0·920, when the fire is extinguished. The injection of steam is, however, continued until oil ceases to come over. The still is then left to cool, and the residue, called *goudron* or *deggut*, is run off while still hot into tanks placed outside the building. The fractions collected by this process present the characteristics given in Table XVIII.

'*Solar Oil*' is too fluid for lubrication, and is used either as a heavy illuminating oil or for making oil-gas. '*Mixing Oils*' are also prepared from solar oil, the chief use of which is for purposes of adulteration (*Redwood*).§

'*Goudron*' when cold is almost solid. It is used as fuel and for other purposes. Sometimes a lubricating grease is made from it, of the nature of vaseline, by mixing it with about one-third solar oil and very gradually heating the mixture in a still to 180°–200° C. Distillation is then started by passing in superheated steam. At first a fluid oil comes over, but soon the distillate begins to partially solidify on cooling, the proportion of solid gradually increasing until the whole solidifies. This distillate is collected separately, until about three-fourths of the contents of the still have come over.

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* *Jour. Soc. Chem. Ind.*, iv. (1887) p. 631.

† See *Jour. Soc. Chem. Ind.*, 1885, p. 111; and 1886, p. 382.

‡ Redwood states that Messrs. Noble have a cylindrical tank of this description holding eleven million gallons.

§ *Petroleum*, vol. i. p. 383.

TABLE XVIII.—FRACTIONAL DISTILLATES FROM RUSSIAN RESIDUUM.

Fraction.	Description.	Distilling at °C.	Per Cent.	Specific Gravity.	Colour.
1st	*Solar Oil*, . .	150–170	10–12	·840–·860	Pale yellow.
2nd	*Light Spindle Oil*, .	170–200	12–15	·870–·880	Yellow.
3rd	*Heavy Spindle or Light Machine Oil*,	200–250	8–10	·895–·900	Yellow.
4th	*Engine Oil*, . .	250–300	30–33	·908–·912	Reddish-yellow.
5th	*Cylinder Oil*, . .	300–320	10–12	·915–·920	Red.
Residue	*Goudron*, . . .	...	12–15	·950	Brown black.

All the *lubricating oil distillates* have a dark colour and a strong odour. Paler coloured odourless oils are produced from them by chemical treatment followed by redistillation, as in the case of the American oils, but as the Russian oils contain no paraffin wax the refrigerating process is, of course, omitted.

The various forms of plant used for the distillation of lubricating oils from petroleum and shale, though differing in detail, merely represent different methods of carrying out the general principles referred to on pp. 90-92, and the yield and characters of the separate fractions obtained in different factories vary according to the nature of the raw material and the demands which the manufacturer has to meet.

(*c*) **Shale Oils.**—Crude shale oil yields on distillation the same products as crude petroleum, viz. :—naphtha, illuminating oil, gas oil, lubricating oil, and paraffin wax. The methods of separating these products and obtaining them in a pure state are the same in principle, viz. :—fractional distillation, followed by chemical treatment of the distillates; but the process is more complicated. Shale oil is subjected to a large number of separate distillations and treatments in order to facilitate the separation of the paraffin wax, of which the crude oil yields about 12 per cent., whilst American petroleum yields only about 2 per cent., and Caucasian petroleum none. The lubricating oils from shale are of low viscosity (spindle oils), and are all *distilled oils*,

being no products corresponding to the natural and reduced oils
red from American petroleum.
r further information regarding the manufacture of mineral
ating oils, drawings of the plant, etc., the reader is referred to
andard treatises on the subject by Redwood and others.

. Properties and Composition of Mineral Lubricating Oils.

neral lubricating oils are classed commercially as ‘pale’ and
.’ The pale oils are more or less transparent, and present a
y of shades of yellow and red. The dark oils are opaque, and
ither greenish- or brownish-black. Most mineral oils, unless
have been ‘debloomed’ by chemical treatment, are (in distinc-
o animal and vegetable oils) fluorescent. The smell and taste,
gh usually slight, are also characteristic.
e specific gravity ranges from 0·860 to 0·920. The boiling-
is high, usually above 600° F. (315·5° C.) in the case of refined
ed oils. The flashing-point ranges, with few exceptions, from
to 600° F. The cold-test or setting-point varies, and depends
upon the proportion of solid hydrocarbons present. Russian
ave the lowest setting-point, sometimes below 0° F.; American
ldom remain fluid below 25° F.; Scotch oils set at about 32° F.
e lubricating oils obtained from petroleum present a much greater
of viscosity than the fixed oils. The thinnest are more fluid
sperm oil; the thickest are more viscous than castor oil. Scotch
oils are only met with among the oils of low viscosity.
ence to the tables on pp. 154–158 will show how slight is the
ction between specific gravity and viscosity. Among oils of a
specific gravity, natural and reduced oils are more viscous than
d oils, and among the latter Russian oils are more viscous than
ican. Mineral oils lose viscosity with rise of temperature more
y than the fixed oils, but if the curves of absolute viscosity on
0 and 161 be studied, it will be seen that this difference becomes
less marked at temperatures above 100° F. (or 150° F. in the case
inder oils). The loss of viscosity is greater the more viscous
l; and the higher the temperature above the normal, the more
do all oils approximate to one another in viscosity. It is not
ly owing to the greater influence of temperature on the vis-
of mineral oils that they are less perfect lubricants than the fixed
ut chiefly owing to the fact that they are deficient in the pro-
of ‘oiliness,’ the nature and cause of which are somewhat obscure.
hough the chemical composition of petroleum has been the
t of an immense amount of research, attention has chiefly been
d to the naphtha and illuminating oil fractions, while those of
boiling-point, from which lubricating oils are prepared, have
omparatively little studied. Allen states* that the lubricating
tained from American petroleum and from shale consist largely

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* *Comm. Org. Anal.*, vol. ii. (2nd edit.), p. 401.

of olefines; paraffins are present in considerably larger proportion in the petroleum product than in the shale product, and the latter also contains small amounts of polymerized acetylenes, and possibly also terpenes. Zaloziecki has confirmed the presence of terpenes in the higher fractions from petroleum.* Aisinmann † states that the American lubricating oils consist chiefly of paraffins, and that those from Baku are composed mainly of naphthenes and olefines. More recently, Engler and Jezioranski ‡ have come to the conclusion that these differences do not exist. By making analyses of petroleums from different sources, and also of the various fractions obtained by their distillation, they have found that the ratio of carbon to hydrogen increases with the boiling-point, and that in all cases the highest fractions contain, in considerable quantity, hydrocarbons which are poorer in hydrogen than those of the ethylene series. From these analyses, and from a comparison of the amount of each fraction absorbed by sulphuric acid, they conclude that the fractions boiling above 200° C., of American as well as of Russian and Galician oils, consist mainly of unsaturated hydrocarbons. Kraemer and Spilker § have prepared synthetical hydrocarbons, resembling in their physical and chemical characters mineral lubricating oils, by the condensation of methylbenzenes with cinnamene or with allyl alcohol in the presence of sulphuric acid. The product formed from pseudocumene and allyl alcohol had the composition $C_{21}H_{28}$, and was probably dimethyldicumylmethane; it boiled above 300° C., and in the viscometer gave, at 15° C., the value 775 (water = 1), whilst the best Russian lubricating oil gave, in the same apparatus, the value 40. Kraemer and Spilker regard these bodies as the 'viscosity carriers' of mineral lubricating oils, and have proved that their viscosity increases rapidly with the number of methyl groups in the molecule. Mills states that the normal paraffins are not lubricants, and that the lubricating properties belong to one or more series of isoparaffins.||

Besides the fluid hydrocarbons, American and Scotch oils contain solid hydrocarbons (paraffin), and in the dark 'reduced' oils variable quantities of asphaltic and tarry bodies exist.

Mineral lubricating oils are unsaponifiable, which enables them to be easily separated from the fixed oils. In Hübl's process they absorb from 7 to 23 per cent. of iodine, according to their origin. Owing to the almost entire absence of any tendency to oxidize or develop acid, they do not gum or corrode bearings, and, if carefully refined so as to be free from volatile hydrocarbons, they undergo but little change by use. Therefore, pure mineral oils, if occasionally filtered to remove suspended impurities, can be used over and over again, which is not the case with any of the fixed oils. Mineral oils,

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* *Jour. Chem. Soc.*, 1894, Abs., i. 611.

† *Jour. Soc. Chem. Ind.*, 1895, p. 283.

‡ *Jour. Chem. Soc.*, 1896, Abs., i. p. 1.

§ *Jour. Chem. Soc.*, 1891, Abs., p. 1462.

|| *Destructive Distillation*, p. 34.

owing to their non-oxidizable character, are also incapable of spontaneous ignition, and when mixed in sufficient proportion with animal and vegetable oils reduce the risk of fire.

B.—FIXED OILS AND FATS.

Sources, Composition, and General Properties.

Fixed oils, so-called because they are not volatile without decomposition, are found ready formed in certain tissues of animals and plants. They differ from the mineral oils in containing oxygen as an essential constituent, the proportion ranging from 9·4 to 12·5 per cent. The distinction between fixed oils and fats is only a matter of temperature. All fixed oils become fats at low temperatures, and all fats become oils at or below 150° F.

The fat of animals is found in the cells of the adipose tissue, or in the blubber of marine animals, from which it is melted out or 'rendered' by simple heat, or by boiling with water. The oils of plants occur mostly in the seeds or fruit, and are obtained either by expression or by means of solvents such as petroleum ether; oils so obtained are frequently subjected to a process of refining, in order to remove the albuminous and mucilaginous matter which is expressed or dissolved out with the oil. Each of the different oil-yielding plants and animals furnishes its own peculiar oil; hence a considerable variety of fixed oils and fats exist.

Animal oils are usually either colourless or yellow; vegetable oils are of various shades of yellow and green, the green colour being due to the presence of *chlorophyll*, which is characteristic of this class of oils. Each kind of oil has usually a distinctive odour by which it can be identified. Fixed oils very rarely present a fluorescent appearance, unless adulterated with mineral oil.

In specific gravity they range from about 0·879 to 0·968. Sperm oil is the least viscous, castor oil the most, but each kind of oil has its own peculiar viscosity, which varies but little. They cannot be distilled without decomposition, the so-called 'boiling' of fixed oils being due to the escape of gases produced by destructive distillation. The setting-points of fixed oils and the melting-points of fats vary considerably (see pp. 191 and 196).

A fundamental difference between fixed oils and mineral oils exists in their behaviour towards atmospheric oxygen. Mineral oils are indifferent to oxygen, but all the fixed oils combine with it,* and most of them undergo, as a result of the oxidation, changes which convert them sooner or later into solid elastic varnishes. The oils which behave in this manner are called 'drying oils,' and a few which oxidize and dry most rapidly (notably linseed oil) are used as paint

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* In consequence of this property, cotton waste and similar fibrous material when saturated with many of the fixed oils, especially those of the drying class, is liable to heat and undergo spontaneous ignition (see page 268).

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oils. Lubricants are selected from the 'non-drying' or less strongly drying oils, the chief of which are olive, rape, and castor among vegetable oils, and lard, neatsfoot, and sperm among animal oils.

All fixed oils are composed of fatty ethers or *esters*, formed by the union of alcohol radicles with fatty acid radicles. The alcohol radicle occurring in the vegetable oils and in most of the animal oils is the trivalent radicle *glyceryl*, C_3H_5, the radicle of glycerol or glycerin ($C_3H_5(OH)_3$), and its esters, known as *glycerides*, may be represented by the formula $C_3H_5R_3$, in which R represents the fatty acid radicle. Usually three or more esters occur together. Thus, tallow contains triglyceryl stearate or stearin $C_3H_5(O.C_{18}H_{35}O)_3$, triglyceryl palmitate or palmitin $C_3H_5(O.C_{16}H_{31}O)_3$, and triglyceryl oleate or olein $C_3H_5(O.C_{18}H_{33}O)_3$. Stearin and palmitin predominate in the solid fats, olein in the fluid oils. Olein is the chief constituent of many of the best known lubricants, such as lard, tallow, neatsfoot, and olive oils.

Allied to the fats are the *waxes*, which are esters of mono- and dihydric alcohols. Thus cetyl palmitate or cetin, $C_{16}H_{33}.O.C_{16}H_{31}O$, derived from cetyl alcohol ($C_{16}H_{34}O$), is the chief constituent of spermaceti, and myricyl palmitate or myricin, $C_{30}H_{61}.O.C_{16}H_{31}O$, from myricyl alcohol ($C_{30}H_{62}O$), is the chief ingredient of beeswax. Sperm and bottlenose oils belong to this group, and are therefore known as liquid waxes, since the esters composing them are not glycerides, but are derived from mono-hydric alcohols.

All fatty esters, by hydrolysis, are split up into alcohols and fatty acids. The change can be effected in several ways; by heating with water under pressure, by heating with sulphuric acid, or by heating with alkalis; but however produced it is known as '*saponification*.' In saponification by heating with water under pressure, both the alcohol and the fatty acid are liberated in the free state. Thus, in the case of olein, the complete change is represented by the following equation:—

$$\begin{array}{ccccccc} C_3H_5(C_{18}H_{33}O_2)_3 & + & 3H_2O & = & C_3H_5(OH)_3 & + & 3C_{18}H_{34}O_2. \\ \text{olein} & + & \text{water} & = & \text{glycerol} & + & \text{oleic acid.} \end{array}$$

This change takes place in steam cylinders when fatty oils are used as lubricants, with the result that the fatty acids set free corrode the metal and form metallic soaps which choke the steam passages.

When saponification is effected by means of an alkali, such as potash or soda, the alcohol alone is set free; the fatty acid combines with the alkali or base forming a *soap*. Thus, when olein is heated with a solution of potash the following change takes place, in the definite proportions stated:—

$$\begin{array}{ccccccc} C_3H_5(C_{18}H_{33}O_2)_3 & + & 3KOH & = & C_3H_5(OH)_3 & + & 3K.C_{18}H_{33}O_2. \\ \left.\begin{array}{c}\text{olein}\\ \text{884·84 pts.}\end{array}\right\} & + & \left\{\begin{array}{c}\text{potash}\\ \text{168·44 pts.}\end{array}\right\} & = & \left\{\begin{array}{c}\text{glycerol}\\ \text{92·06 pts.}\end{array}\right\} & + & \left\{\begin{array}{c}\text{potassium oleate}\\ \text{961·22 pts.}\end{array}\right. \end{array}$$

This reaction enables us to at once distinguish between a mineral oil and a fixed oil, and to separate the mineral oil from a mixture of the two. For, on boiling with potash, the hydrocarbons composing the mineral oil undergo no change, but the esters composing the fatty oil undergo saponification, forming soaps and glycerol, both of which can be washed away by water, leaving the mineral oil in the free state.

In the case of a wax like sperm oil or wool fat a complication arises, since the wax alcohols are not soluble in water, and, therefore, contaminate the mineral oil. The mixture can, however, be analysed by the method described on page 233.

Soaps are easily decomposed by mineral acids, and the fatty acids are set free. Thus, in the case of potassium oleate and hydrochloric acid :—

$$\underset{\text{potassium oleate}}{K.C_{18}H_{33}O_2} + \underset{\text{hydrochloric acid}}{HCl} = \underset{\text{potassium chloride}}{KCl} + \underset{\text{oleic acid.}}{C_{18}H_{34}O_2}.$$

Most fatty acids, when melted, are oily liquids, which float as an insoluble oily layer on the surface of water; but a few, such as the valeric acid of porpoise jaw oil, are soluble in water, and evaporate with the steam when the water is boiled. The fatty acids obtained by saponifying the natural oils are almost invariably mixtures, and by examining the mixed fatty acids it is frequently possible to determine the nature of the fatty oil from which they have been derived.

The chief fatty acids which are known to occur in lubricating oils are given in Table XIX. (p. 102).

The *vegetable oils* chiefly used for lubrication are rape, olive, and castor. Rape and olive oils are employed both alone and mixed with mineral oils. Castor oil is largely used for railway work in India, mixed with heavy mineral oil, of which it can take up a certain proportion only, the amount varying with the temperature. To produce with castor oil and mineral oil a mixture that will not, even at low temperatures, separate on standing, an equal volume of tallow oil or lard oil must first be mixed with the castor oil. Coconut oil is said by Hurst to be used in India on light-running machinery, and in this country for the preparation of mixed spindle and loom oils, but it seems quite unsuitable for such purposes (see p. 111). Maize oil (corn oil) has been described as a non-drying oil and a good lubricant, but Archbutt has found that it dries as readily as cottonseed oil.* Palm oil is sometimes used in making the yellow grease employed for the lubrication of railway wagon axles.

The *animal oils* chiefly employed for lubrication are tallow, tallow oil, lard oil, neatsfoot oil, whale oil, sperm oil, and porpoise jaw oil. Tallow is used for grease making, and the four following oils are chiefly employed for mixing with mineral oils. Sperm oil is used, both mixed and unmixed, for light machinery and spindles. Porpoise jaw oil is used for the lubrication of watches and delicate mechanism, for which a thoroughly non-drying and fairly limpid oil is required.

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* *Jour. Soc. Chem. Ind.*, xviii. (1899), p. 346.

TABLE XIX.—FATTY ACIDS OCCURRING IN LUBRICATING OILS.

Series.	Name of Acid.	Formula.	Occurs chiefly in
Acetic $C_nH_{2n}O_2$	Isovaleric	$C_5H_{10}O_2$	Porpoise jaw oil.
	Caproic	$C_6H_{12}O_2$	Coconut oil.
	Caprylic	$C_8H_{16}O_2$	
	Capric	$C_{10}H_{20}O_2$	
	Lauric	$C_{12}H_{24}O_2$	
	Myristic	$C_{14}H_{28}O_2$	
	Palmitic	$C_{16}H_{32}O_2$	Palm oil; also tallow, olive oil, and coconut oil.
	Stearic	$C_{18}H_{36}O_2$	Tallow; also palm, castor, and rape oils.
	Arachidic	$C_{20}H_{40}O_2$	Earthnut, rape, and mustard oils.
	Lignoceric	$C_{24}H_{48}O_2$	
Oleic $C_nH_{2n-2}O_2$	Oleic	$C_{18}H_{34}O_2$	Olive oil and the animal oleins.
	Rapic	$C_{18}H_{34}O_2$	Rape oil.
	Erucic	$C_{22}H_{42}O_2$	
Linolic $C_nH_{2n-4}O_2$	Linolic	$C_{18}H_{32}O_2$	The drying oils; also in olive and palm oils.
Ricinoleic $C_nH_{2n-2}O_3$	Ricinoleic	$C_{18}H_{34}O_3$	Castor oil.
	Ricinisoleic	$C_{18}H_{34}O_3$	
$C_nH_{2n}O_4$	Dihydroxy-stearic	$C_{18}H_{36}O_4$	Castor oil.

Rape (Colza) Oil.—Commercial rape or colza oil is obtained from the seeds of several cultivated varieties of *Brassica Campestris*, Linn., the navew or wild turnip, a plant belonging to the natural order *Cruciferae*, cultivated very extensively in France, Germany, Austria-Hungary, Roumania, and Southern Russia; also in India and China. The principal source of European rape oil (German, rapsöl) is rape seed or cole seed, from *B. Campestris* var. *Napus*. *B. Campestris* proper, cultivated in France and Belgium under the name 'colza,' yields colza oil (German, kohlsaatöl), and *B. Campestris* var. *Rapa* (*B. Rapa oleifera*, Linn.), grown in South Germany, yields the oil known as 'rubsen' (German, rüböl or rübsenöl). These three oils, colza, rape, and rubsen, though botanically quite distinct, are similar in their chief physical and chemical characters, and are not distinguished commercially, being all sold as rape oil.

The rape seed which is so largely imported into Europe from India for the manufacture of rape oil is the product of chiefly *B. Campestris* var. *Glauca.* Indian rape seed varies very much in size and appearance, according to the district in which it has been grown, the finest commercial varieties being known as yellow Guzerat and yellow Cawnpore, less esteemed kinds as Madras, brown Calcutta, brown Cawnpore, Ferozepore, etc. A seed known as Jamba rape,* which is said to yield a good oil, is occasionally exported from Kurrachi. Indian rape has some of the characters of mustard (possibly owing to the common practice of sowing the seeds together), in consequence of which the cake cannot be safely used for feeding cattle.† The resemblance between some kinds of Indian rape seed and white mustard seed has led to frequent mistakes and even lawsuits. Thus the seed known as 'Guzerat' resembles a mixture of ordinary rape with white mustard. The careful examination of Dr Wittmack, of the Berlin Agricultural Museum, however, has shown conclusively that the structural characters of the seeds are those of rape and not of white mustard, and there is reason to suppose that the white as well as the dark seeds are all the produce of the same plant.‡ Watts§ mentions two other varieties of Indian rape, viz.:—*B. Campestris* var. *Dichotoma* and *B. Campestris* var. *Toria*; the oil from the former he terms Indian colza, and says it is chiefly used for anointing the body, that from the latter is probably mixed with the oil from the var. *Glauca.* The following results may be of interest as showing the characters of Indian rape oil extracted from the seed by ether in the laboratory:—

TABLE XX.

DESCRIPTION OF SEED.	Yellow Guzerat.	Brown Calcutta.	Madras.
Sp. gr. at 60° F., ...	0·9133	0·9146	0·9140
Saponification value, per cent.,	17·50	17·42	17·45
Iodine value, per cent., . .	97·8	102·7	99·6
Oxidation test (see p. 255), .	1 grm. of the oil did not dry or become unduly thickened in 16 hrs. at 212° F.		

Rape seed, from *B. Campestris* var. *Chinensis* (Chinese Cabbage), is cultivated extensively in China, and another variety, *B. Campestris* var. *Cernua*, in Japan. The oil of the hedge or wild radish, *Raphanus Raphanistrum*, sometimes called hedge mustard, is said to be mixed with and even substituted for rape oil in Hungary.

Rape oil is obtained from the seed either by expression or by extraction with solvents. In either case the seed is first thoroughly crushed in roller mills. In the process of expression the crushed seed is first subjected to very moderate pressure in the cold, by which a considerable quantity of oil is obtained; the cakes are again passed through the mill, and the meal is then heated and damped in a jacketed steam-pan called a 'kettle,' which process, by rendering the remaining oil more fluid, facilitates its expression, and at the same time coagulates some of the albuminous matter of the seed and prevents it from being expressed with the oil. The heated seed-meal is then rapidly moulded into cakes and subjected to hydraulic pressure. In the process of extraction with a solvent, by which means the larger proportion of the rape oil of commerce is now obtained, the crushed dry seed is placed in the extraction apparatus and exhausted with petroleum spirit, carbon disulphide, or ether, and the oil is obtained by distilling off the solvent.*

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* For its characters see Lewkowitsch, *Analysis of Oils*, p. 413.

† *Kew Bulletin*, 1894, p. 96.

‡ *Kew Bulletin*, 1877, p. 84; and 1894, p. 96.

§ *Dict. of the Economic Products of India*, vol. i. pp. 522–528.

Crude rape oil is dark in colour, and contains albuminous impurities which cause turbidity and set up fermentation, resulting in the partial decomposition of the glycerides with liberation of free fatty acids. In order to remove these impurities, it is usual to refine the oil by agitating it whilst warm with a strictly limited proportion (0·5 to 1·5 per cent.) of sulphuric acid (Thénard's process) sufficient to attack and char the impurities, which are more easily acted upon, without causing serious hydrolysis of the glycerides. After thoroughly agitating the oil with the acid for about ¾ to 1 hour, sometimes longer, according to the quantity and quality of the oil treated, the mixture is allowed to rest, and the suspended acid and impurities gradually settle out as a dark coloured magma ('foots'), leaving the oil bright and clear. The latter is then drawn off, washed by agitation with steam and hot water, again racked off and boiled with water a second time, allowed to settle, and 'baled' until bright.

The following results are of interest as showing the effect of the acid refining process upon the acidity and other characters of rape oil. For the samples the authors are indebted to Mr. John F. Hutcheson of Glasgow, who kindly obtained them specially from Stettin.

TABLE XXI.—EFFECT OF REFINING RAPE OIL BY THÉNARD'S METHOD.

DESCRIPTION.	Brown Rape Oil from freshly crushed seed.	Brown Rape Oil clarified by settling.	Refined Rape Oil.
Free (oleic) acid, per cent., .	1·58	0·98	2·26
Specific gravity at 60° F., .	0·9146	0·9147	0·9141
Comparative viscosity at 60° F.,	104	101	100
Saponification value, per cent.,	17·42	17·36	17·30
Iodine value, per cent., . .	101·8	100·9	102·3
Maumené thermal value, °C.,	57·0	56·25	56·75
Unsaponifiable matter, per cent.,	0·98	0·95	0·75

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* For a detailed description of oil mill plant, see *A Practical Treatise on Animal and Vegetable Fats and Oils*, by W. T. Brannt, vol. i. chaps. x. and xi.

Archbutt has found traces of free sulphuric acid in rape oil refined at Stettin and also at Hull (see p. 301).

As the tendency of the acid refining process is to increase the acidity of the oil, an alkaline process would appear preferable. Everard's process, which consists in agitating the oil with a weak solution of caustic soda, has been applied to rape oil. One difficulty in the practical working of such processes is the tendency of the oil and alkaline liquor to form emulsions which are troublesome to separate, and to avoid this it has been proposed to use a liquid formed by melting soda crystals in their water of crystallization (*Hageman*) which is said not to emulsify. Milk of lime and calcined magnesia have also been suggested.

Rape oil has been found to consist chiefly of the glycerides of stearic, rapic, and erucic acids, but the high iodine value of the oil points to the presence of an acid of the linolic or linolenic series. Genuine rape oil also contains a small and variable proportion of arachidic and, probably, lignoceric acids. Ponzio[*] found 0·4 per cent. of arachidic acid in one sample. Alén[†] found arachidic acid in the oil from Guzerat seed, but not in that from the European varieties; he used Souchère's method.[‡] Archbutt,[§] by Renard's method (see p. 273), found 1·43 per cent. of arachidic (and lignoceric) acids in rape oil extracted by means of ether from Guzerat seed, and 1·14 per cent. in commercial (Stettin) rape oil expressed from rape and rubsen seed. Of 51 samples of commercial rape oil which were specially examined by Renard's process, about two-thirds were found to contain arachic acids. Indian rape oil from *B. glauca*, seems to contain more of these acids than the European oil, and the extracted oil more than the expressed oil; of the latter, the cold-pressed oil probably contains less than the hot-pressed. These acids are also contained in mustard oil.

Rape oil is by no means a non-drying oil, and as different samples vary considerably in oxidizing property, it is necessary to make a careful selection of the oil intended for lubricating. Rape oil is not suitable for delicate machinery.

According to Schaedler, rape oil sets or solidifies at – 2° to – 10° C.; but Holde states that all rape oils sooner or later solidify at 0° C. (32° F.). The result of the following experiment does not support Holde's statement. Some genuine refined Stettin rape oil was placed in a glass tube, immersed in melting ice for 3 hours without stirring, and then for 3 hours longer, stirring at intervals. It remained clear and fluid. Some of the same oil, previously frozen, having been added, the oil was kept in ice for 3 hours longer, with occasional stirring, but the frozen oil slowly melted. The temperature was then gradually reduced to 14°–16° F. (– 10° to –9° C.), and the oil became very turbid, but after remaining for 2 hours at this temperature, with stirring, it did not lose its fluidity. After still further reducing the temperature to 11° F. (– 11·6° C.), and stirring, the oil solidified in about half an hour.

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[*] *J. für pr. Chem.*, 48 (1893), p. 487.

[†] *Svensk. Kemisk Tidskrift*, 1893, p. 179.

[‡] Lewkowitsch, *Analysis of Oils*, p. 445.

[§] *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1009.

Black Sea Rape Oil. Ravison Oil.—In the countries bordering the Danube and Black Sea, colza grows both wild and under cultivation.* Oil expressed from the seed of the Black Sea district, known as ravison oil, is inferior in quality to, and much cheaper than, ordinary rape oil; it has a higher sp. gr., higher saponification and iodine values, and more strongly drying properties than ordinary rape oil, and is usually of bad quality for lubricating. The unacknowledged admixture of this oil with rape oil must therefore be regarded as adulteration. The chief properties of the oil are shown by the results in Table XXII. The samples of Black Sea oil and seed were kindly supplied by Messrs. Seaton & Co., of Hull.

Olive Oil.—Olive oil is obtained from the fruit of the cultivated olive tree, *Olea Europæa Sativa*, the numerous varieties of which are grown chiefly in the countries bordering the Mediterranean, also in California and other countries where the climate is suitable. The fruit is very rich in oil, which is contained chiefly in the fleshy mesocarp, but also in the kernel and shell (endocarp).

The finest olive oil is obtained † by hand picking the olives before they become too ripe, gently pressing them by hand in cloths and collecting the oil which exudes. The limited quantity of '*virgin oil*' thus obtained appears to be used as salad oil, and some of it as a lubricant by watchmakers; it is purified by agitation with water, allowing the mucilaginous matter to subside, and skimming off the clear oil from the surface. Oil nearly as fine is obtained on the large scale by crushing the ripe olives under millstones or between iron rolls, usually, though not always, without breaking up the kernels, and pressing the pulp, without heating it, in bags of esparto grass under very moderate pressure; after purifying by agitation with water and settling, this cold-pressed oil is called '*superfine oil*,' or frequently '*virgin oil*,' and is used chiefly as a salad oil. The once-pressed marc is broken up, stirred with hot water, and again pressed, more strongly than before, yielding '*ordinary oil*,' which is said to be but slightly inferior to the cold-pressed oil. The twice-pressed marc, after being stored for a time and allowed to ferment (which facilitates the extraction of the oil), is reground so as to crush the olive stones, and after being stirred up with boiling water is subjected to the heaviest pressure obtainable with the appliances used; oil of inferior quality, called '*pyrene oil*' or '*bagasses oil*,' is thus obtained. The residual marc still contains some oil, which is extracted by means of carbon disulphide or petroleum spirit and is known as '*sulphocarbon oil*.' The last two kinds of oil are dark green or brown in colour (due to the presence of chlorophyll), consist largely of decomposition products, are very acid, and are fit only for soapmaking or dyeing. Some of the dark-coloured oils, even when nearly neutral, are of inferior quality for lubricating, owing to their tendency to thicken and 'gum' on the bearings. Oils known as '*huile tournante*' and '*huile d'enfer*' are much decomposed and highly acid olive oils recovered from residues,

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* Spon's *Encyclopædia*, vol. iv. p. 1385.

† Spon's *Encyclopædia*, vol. iv. p. 1397; Alder Wright, *Oils, Fats, and Waxes*, p. 343.

TABLE XXII.—PROPERTIES OF BLACK SEA RAPE OIL.

PHYSICAL AND CHEMICAL DATA.	Kustendje Rape Oil made from Wild Rape Seed from the Black Sea. Extracted by the CS_2 process.	Black Sea Rape Oil Expressed and Refined. 2 Samples.		Oil extracted in the Laboratory from Black Sea Rape Seed. 2 Samples.		Oil extracted from Seed (*b*) after picking out 13·3 °/o of Foreign Seeds.
		(*a*)	(*b*)	(*a*)	(*b*)	
Free acid, as oleic acid, °/o	2·43	6·02	2·8	..	..	..
Sp. gr. at 60° F.,	0·9183	0·9200	0·9217	0·9211	0·9200	0·9200
Viscosity at 60° F.,	About 6 °/o lower than that of refined Stettin rape oil.	About 13 °/o lower than that of refined Stettin oil.				
Saponification value, °/o	17·79	17·93	17·89	17·93	17·81	17·81
Iodine value,	110·2	110·7	121·7	111·5	108·9	109·3
Maumené thermal value °C.,	65·8	76	..	..	..	..
Unsaponifiable matter, °/o	1·45	1·66	1·64	..	..	..
Arachic acids obtained by Renard's process,	0·79 °/o (m.p. 70·4° C.)	..	..	..	..	..
Colour Reactions.						
Milliau test,	neg.	neg.	neg.	..	..	..
Badouin's test,	..	..	neg.	..	..	..
Oxidation test. (1 grm. of oil exposed on a watch glass at 212° F. for 16 hrs.),	Rather more dried than Stettin oil, but not more thickened.	Badly dried and much more thickened than Stettin oil.	..	Dried and much thickened.		
Properties of Mixed Fatty Acids.						
Sp. gr. at $\frac{212°}{212°}$ F.,	..	..	0·8802			
Iodine value,	..	..	126·1			

For the constants of genuine rape oil, and the detection of adulteration, see p. 301.

and, though in demand for dyeing Turkey red, are quite unfit for lubricating.

In the refining of the crude olive oil, it is sometimes allowed merely to rest in large tanks until the 'mucilage' has deposited, undergoing during the time more or less decomposition, and often becoming spoiled for lubricating. Sometimes the oil is refined by washing with water alone, and sometimes it is washed with caustic soda.

Olive-kernel Oil was lately believed to be quite different in properties from ordinary olive oil (the oil of the mesocarp), having a sharp and bitter taste, a dark green or brown colour, and being readily soluble in alcohol, owing to the presence of much free fatty acid; but it has been shown by Klein* that the characteristics hitherto assigned to olive-kernel oil are really those of *pyrene* oil or *bagasses* oil, the dark coloured and more or less decomposed oil expressed from the stones and refuse of the first and second pressing of the olives. Pure olive-kernel oil, prepared both by cold and by warm expression from the kernels alone, without any admixture of the pulp, was found to have the following characters as compared with a sample of bagasses oil:—

	Olive-kernel Oil.	*Bagasses Oil.*
Sp. gr. at 60° F., . . .	0·9186 to 0·9191	0·928
Saponification value, %, . .	18·23 ,, 18·38	19·05
Iodine value, . . .	87·0 ,, 87·8	71·6
Free fatty acids, %, . .	1·00 ,, 1·78	71·12

From these results it appears that pure olive-kernel oil is somewhat higher in specific gravity and iodine value, and lower in saponification value, than ordinary olive oil, but it does not naturally contain an excess of free fatty acids. The characters of olive oil will, it is evident, depend to some extent upon whether the process of extraction has or has not been such as to include the kernel oil.

Olive oil contains about 28 per cent. palmitin, 67 per cent. olein, and 5 per cent. linolein (*Hazura*). Stearin is absent (*Hehner* and *Mitchell*). Traces only of arachin have been found in genuine olive oil, and Klein states that in olive-kernel oil he could find none.

For the characters of genuine olive oil and the detection of adulteration, see p. 305.

Castor Oil.—Castor oil is obtained from the seeds of the castor oil plant, *Ricinus communis*, Linn., of which there are numerous varieties. The plant is indigenous to India, but is also cultivated extensively in the United States, France, Italy, Algeria, etc. It grows wild in Formosa,† and the oil is for the most part wasted; but in Java the plant is cultivated, and the export of castor oil is likely to become an important industry.‡ Two varieties of the plant are recognised by Indian cultivators, one small-seeded and the other large-seeded. The oil from the former is the most highly esteemed, and is chiefly used for medicinal purposes; it is expressed from the crushed seed without the aid of heat ('cold-drawn'), and after careful refining by heating with water is straw-yellow to greenish-yellow in colour, and nearly odourless. The oil for lubricating and burning is mostly got from the large-seeded kind, and is expressed partly cold and partly hot. The crude oil is refined by boiling it with water; soluble matters (starch, gum, etc.) are dissolved, and albumen is coagulated; the oil is then clarified by filtering or settling. In India an ancient process, which still survives, consists of first roasting the seeds to coagulate albuminous matters and facilitate the extraction of the oil, subsequently crushing, boiling with water, and skimming off the oil which rises to the surface. Oil thus obtained is often very dark in colour, and odorous. It is sometimes exported in this condition, at others it is bleached by exposure to the sun, treated with charcoal, and filtered through flannel or paper.*

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* *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1055; *Analyst*, xxiii. (1898), p. 284.

† *Jour. Soc. Chem. Ind.*, xii. (1893), p. 769.

‡ *Ibid.*, xiv. (1895), p. 321.

Castor oil consists almost wholly of triricinolein, the glyceride of two isomeric hydroxylated acids, ricinoleic and ricinisoleic ($C_{18}H_{34}O_3$). Small quantities of tristearin and of the glyceride of dihydroxystearic acid ($C_{18}H_{36}O_4$) are also present, but neither palmitin nor olein.†

Castor oil, in very cold weather, is liable to deposit a solid fat, but it congeals only at very low temperatures. It does not readily dry on exposure to the air, but turns rancid by oxidation.

Owing to its peculiar composition, castor oil differs remarkably in solubility from most fixed oils. Thus it is easily soluble in alcohol (other oils being but sparingly soluble), and it is almost insoluble in petroleum spirit and in mineral burning and lubricating oils (in which other fixed oils are easily soluble). The ready solubility of castor oil in alcohol has been made the basis of a valuable test for the presence of adulterants in this oil (see p. 308).

The limited extent to which castor oil and mineral oils are mutually soluble is of importance in the preparation of mixed lubricants containing the former. At 59° F. (15° C.) castor oil is practically insoluble in petroleum spirit and in burning oil. In '865' Scotch shale oil, at the same temperature, it dissolves to the extent of about 1–1½ per cent.; '890' shale oil dissolves about 2–2½ per cent. of it; and '907/12' American mineral oil dissolves rather more. Therefore, at the ordinary temperature, castor oil is very sparingly soluble in mineral oils; the solubility is greater the more dense and viscous the mineral oil, it increases with rise of temperature and diminishes as the temperature falls.

On the other hand, castor oil is able to dissolve mineral spirit and mineral oils in proportions which decrease as the sp. gr. of the mineral oil increases. The following table shews the maximum volumes which were found to give a clear solution at 59° F. (15° C.) with 10 c.c. of pure castor oil.

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* *Jour. Soc. Chem. Ind.*, xii. (1893), p. 770.

† Lewkowitsch, *Analysis of Oils*, p. 420.

TABLE XXIII.

MINERAL OIL EMPLOYED.	Sp. Gr. at 60° F.	Maximum Volume miscible with 10 c.c. of pure Castor Oil at 59° F.
Mineral (petroleum) spirit,	0·692	9·2 c.c.
'White Rose' petroleum,	0·788	5·5 c.c.
Scotch shale oil,	0·865	3·7 c.c.
" "	0·890	2·45 c.c.
American pale mineral oil,	0·907–0·912	1·7 c.c.

Although pure castor oil thus almost refuses to mix with mineral lubricating oil, the difficulty entirely disappears if a third oil, such as rape, tallow, or lard oil, is present, a clear mixture of the three being readily obtained. Pure castor oil mixes with refined rosin oil in all proportions.

Palm Oil.—Palm oil or fat, which is used to a limited extent for making railway wagon grease, is obtained from the fleshy covering (mesocarp) of the fruit of the oil-palms, *Elais guineensis* and *E. melanococca*, which flourish in West Africa. The fruit is gathered by the natives and stored in holes in the ground until the pulp has become softened by decomposition; it is then pounded, and after the kernels have been separated the pulp is heated with water until the oil begins to exude; it is then squeezed in rough nets, and the oil which runs out, mixed with more or less fibre, dirt and water, is collected, and forms the palm oil of commerce. It is not surprising that the fat prepared in this crude fashion is much decomposed, and consists, always largely, often chiefly, of free fatty acid. It is on that account a most unsuitable material for making lubricating grease. According to de Schepper and Geitel,* the most neutral brands are the following: Lagos, Loando, Old Calabar, Gold Coast, Sherboro, and Gaboon. The percentage of neutral fat ranges from 58–68 per cent. in the first-named to 79–93 per cent. in the last-named brand.

Palm oil is, at ordinary temperatures, a soft fat, melting at 80°–97° F. when fairly rich in neutral fat; the presence of much free fatty acid may, however, raise the melting-point to 108°–109° F. The chief constituents are free palmitic acid, palmitin and olein, with small quantities of linolein, stearin and another fat. The colour varies from yellow to deep red. The odour of the fresh fat is pleasant and quite characteristic.

Palm Nut Oil.—Palm-kernels contain an oil or soft fat which is quite different from palm oil. In chemical composition and characters it closely resembles coconut oil, having an exceptionally high saponification value (24·8–25·0 per cent.) and a very low iodine value (10–17·5 per cent.). It does not appear to be used as a lubricant.

Coconut Oil.—Coconut oil is obtained from the white pulp of the common coconut, the seed of the coconut palm *Cocos nucifera*, which flourishes abundantly in the tropical Pacific islands, the West Indies, tropical America, etc. The oil is obtained either by expression from the more or less decomposed pulp (native method), or by expression and extraction with a solvent from the dried pulp ('copra') which is imported into Europe for the purpose. The chief use of the oil is for candle and soap-making, but, according to Hurst, it is used as a lubricant for light-running machinery in India, and in this country is employed in admixture with mineral oil as a lubricant for spindles and looms. A brief description of the oil is therefore necessary.

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* Lewkowitsch, *Analysis of Oils*, p. 519.

Commercial coconut oil is at ordinary temperatures in this country a soft white fat, melting to a limpid oil at 68°–82° F., and usually containing a more or less considerable quantity of free fatty acids, ranging from 5 per cent. to as much as 25 per cent., according to Lewkowitsch. It does not, therefore, possess the properties of a desirable lubricant. Coconut oil has a complex and unusual composition, consisting largely of the glycerides of lauric and myristic acids, with some palmitic and oleic, and a notable proportion of volatile acids, caproic, caprylic, and capric; consequently, except from palm-nut oil, which it very closely resembles, it differs remarkably from other oils and fats.

Tallow.—Tallow is the fat of certain ruminant animals, separated by the process of melting or 'rendering' from the enveloping membrane of the tissue. Beef tallow is obtained from oxen, mutton tallow from rams, ewes, bucks, and she-goats.

The rendering of the fat on a small scale is effected by heating the tissue, either alone or with the addition of water, in an open pan over a fire, continually stirring to prevent burning, until the membrane has shrunk together and can be strained off; preferably, the pan is heated by means of a steam-jacket, which admits of more perfect control of the temperature. On a larger scale, a more complete separation of the fat from the tissue is effected by heating the latter in strong closed digesters, into which live steam under a pressure of 50–70 lbs. per square inch is admitted, and the liberated oil which rises to the surface of the condensed water is drawn off through a cock. Another method consists in boiling the fatty tissue in open vessels with water containing sulphuric acid or caustic soda, by either of which the nitrogenous membrane of the cell walls is chemically broken down and the fat liberated. The use of sulphuric acid would be objectionable in rendering tallow intended for lubricating, because it causes partial hydrolysis of the glycerides and increases the proportion of free fatty acids; but the employment of caustic soda, which neutralizes and dissolves the fatty acids, would be advantageous. In rendering tallow for lubrication, the main points to be attended to are to use only fresh fat, which has not had time to undergo decomposition, and to perfectly remove, by settling and straining, all water and fragments of membrane which, by subsequent decomposition, might cause the resulting tallow to develop acidity.

Neutral tallow consists almost exclusively of stearin, palmitin, and olein, and is softer in proportion to the amount of olein it contains. The latter, in genuine tallow, can be measured by the iodine value; for since pure olein absorbs 86·0 per cent. of iodine, and stearin and palmitin absorb none, the iodine value of the tallow × $\frac{100}{86}$ is approximately the percentage of olein. The relative proportions of stearin, palmitin, and olein in tallow vary according to the nature of the animal, its sex, breed, age, food, and the part of the body from which the fat is taken. The fat from the male is usually harder than that from the female, and mutton tallow is, as a rule, harder than beef tallow; but, taking the average, the proportion of olein in tallow is about 46 per cent., and the remainder consists of stearin and palmitin in about equal proportions.

Of the various descriptions of tallow (Russian, North American beef, South American beef, Australian beef, Australian mutton, home refined, etc.), average South American beef is, according to experiments by Deering and by Archbutt, the least acid (see p. 203), and, therefore, when genuine, the best adapted for lubrication and for general application to metal; but there is no reason why preference should be given to any particular brand, if the results of chemical and physical tests prove the tallow to be of good quality.

Tallow Oil.—Tallow at the ordinary temperature of, say, 60°–80° F., is a mechanical mixture of solid and fluid fats, in which the former predominate to a sufficient extent to give the appearance of solidity to the whole. If subjected to pressure, the fluid portion can be squeezed out, and is known as '*tallow oil*'; the solid press-cake forms '*tallow stearine*,' and is used in the candle manufacture. The separation is facilitated by allowing the melted tallow to cool very slowly, without disturbance, in large tubs at a temperature of 70°–80° F.; the crystallization of the solid portion then takes place in small granular particles resembling seeds, whence the process is known technically as 'seeding.' Some of the fluid portion drains through coarse flannel cloth placed upon perforated diaphragms near the bottoms of the tubs, the remainder is obtained by subjecting the semi-solid residue to pressure in canvas bags, as in the manufacture of lard oil (*q.v.*).

Tallow oil differs, therefore, from tallow chiefly in the proportion of olein which it contains, and this proportion, and therefore the setting-point and some other characters, such as the iodine value, must vary according to the temperature at which the oil has been expressed.

Tallow oil, as a lubricant, is used chiefly for mixing with mineral oils to increase the property of 'oiliness,' in which the latter are naturally deficient.

Lard Oil.—Lard oil, expressed from rendered pig's fat or lard, is prepared in a similar manner to tallow oil. The more or less chilled lard is placed in close-textured woollen bags between wickerwork, and is subjected to moderate but long-continued hydraulic pressure (about 10 cwts. per square inch for 18 hours). As in the case of tallow oil, the solidifying-point and other characters of the oil depend upon the temperature at which it has been expressed, winter-pressed lard oil containing less of the solid constituents of the lard than that expressed in warmer weather.

Prime lard oil is a nearly colourless, pale yellow or greenish coloured oil, highly esteemed as a lubricant, and consisting of olein with variable proportions of stearin and palmitin. The viscosity is the same as that of olive oil. The setting-point may vary from about 40° F. (4·4° C.) to several degrees below the freezing-point of water.

Neatsfoot Oil.—Neatsfoot oil is obtained by boiling the feet and hocks of oxen with water. The feet are first skinned * and slit longitudinally with a knife, which is passed between the sections of the hoof and continued between the long bones. A small mass of fat found near the hoof is scooped out with the knife and set apart for the preparation of the best quality of oil (see below). The hoofs are washed in cold water, and then boiled with water in open pans over a fire; the oil which rises to the surface of the water is skimmed off, and forms an inferior grade of neatsfoot oil. After about 3 hours' boiling, the tissues between the horny hoof and the last digit bone are sufficiently softened to allow of the latter being easily scooped out of the hoof with a knife. These 'cores,' consisting of bone, gelatinous matter, and fat, together with the small mass of fat found near the hoof referred to above as being separated before boiling, are put into a separate pan of fresh water and boiled together for the extraction of the best kind of neatsfoot oil. Ten neat's feet yield from 2 to 2½ pints of a pale yellow, nearly odourless oil, which, on standing in a cold place, deposits a solid fat. The portion which remains fluid at a low temperature is used as a lubricant for clocks. Neatsfoot oil was formerly much esteemed and largely employed as a lubricant for engines and heavy machinery; it is now used, like lard and tallow oils, chiefly for mixing with mineral lubricating oils. The extensive demand for neatsfoot oil in the leather trade has probably diminished its employment as a lubricant.

Whale Oil.—Whale oil proper is obtained from the blubber of the Greenland or Arctic 'right' whale, *Balæna mysticetus*; but commercial whale oil includes the oil from the Southern right whale, *Balæna Australis*, and various other species of *Balæna* and *Balænoptera* (fin-backed whales) belonging to the tribe of *Balænoidea* or whalebone-yielding whales.

The oil which naturally exudes from the blubber of these animals, and which is also obtained by heating it with water, is mainly glyceridic in character, and may be distinguished at once from the sperm oils by its high specific gravity (above 0·919), and by yielding less than 4 per cent. of unsaponifiable matter. Whale oil even of the best quality has marked drying properties, and, as a lubricant, is only fitted for very rough work; it is used, however, to some extent for mixing with mineral lubricating oil.

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* Spon's *Encyclopædia*, vol. iv. p. 1368.

Sperm Oil. Arctic Sperm (Bottlenose) Oil.—These oils, obtained from two different kinds (genera) of whale belonging to the family *Physeteridæ* (toothed whales possessing no functional teeth in the upper jaw) are so similar in composition and general characters that they may conveniently be described together. True sperm or 'southern sperm' oil is obtained from the head-cavities and blubber of the Cachelot or great Sperm Whale, *Physeter macrocephalus* (sub-family, *Physeterinæ*), formerly found in all seas up to 70° northern and southern latitudes, but now more scarce and confined chiefly to the Pacific and Indian oceans. Arctic sperm or bottlenose oil is obtained from the much smaller Bottlenose whale, *Hyperöodon rostratus* (sub-family, *Rhynchoceti*), which is caught principally in the Arctic seas between Iceland and Spitzbergen. Both crude oils contain spermaceti—sperm oil much more than bottlenose—which crystallizes out on cooling; it is separated by straining the oil through bags, and is used for the manufacture of sperm candles. Sperm oil is therefore liable to deposit spermaceti unless it has been bagged at a very low temperature. Allen states that practically the whole of the spermaceti is deposited by cooling the oil to 4° C. (39·2° F.).

Neither sperm nor bottlenose oils contain glycerides; they consist entirely of the esters of mono-hydric alcohols, and are, therefore, chemically classed as fluid waxes. According to Lewkowitsch,* the nature both of the alcohols and of the fatty acids is at present unknown.

Sperm oil is pale yellow in colour, and when of good quality has only a faint odour; bottlenose oil is usually darker in colour than sperm oil, and has a more or less unpleasant odour and flavour. Allen has pointed out, as a reason for this, that whilst the blubber of the sperm whale is commonly boiled down for the extraction of the oil on board ship, immediately after the capture and death of the animal, the blubber of the bottlenose whale is brought home in tuns to be boiled down on shore, and has therefore undergone more or less decomposition before the oil is extracted. This difference in the treatment of the bottlenose blubber might be expected to increase the acidity of the oil, but, from the published results, the difference is not great (see p. 203). Allen states that bottlenose oil, if refined with alkali, besides being rendered neutral, loses much of its unpleasant odour and becomes straw-yellow in colour. Deodorized Arctic sperm oil is now an article of commerce.

The low viscosity of sperm and bottlenose oils at 60° F. distinguishes them from many other fixed oils. With rise of temperature both oils maintain their viscosity better than other fixed lubricating oils; but the statement frequently made that the difference is sufficient to account for the superiority of sperm oil as a lubricant is, except as regards castor oil, an exaggeration. This will be made apparent by a comparison of the following series of ratios, which have been calculated from the results in Table XXXIV. (pp. 154–157).

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* *Analysis of Oils*, etc., p. 615.

TABLE XXIV.—RATIOS OF VISCOSITY OF SPERM, OLIVE, AND RAPE OILS.

OIL.	60° F.	100° F.	150° F.	212° F.
	Comparative times of efflux.			
Sperm, ...	100	46·5	25·8	18·1
Olive, ...	100	38·6	17·3	9·9
Rape, ...	100	39·4	17·6	9·8
	Comparative viscosities.			
Sperm, ...	100	44·5	20·2	11·0
Olive, ...	100	37·4	15·3	6·9
Rape, ...	100	37·7	15·8	7·2

Porpoise Jaw Oil; Dolphin (Blackfish) Jaw Oil and 'Melon' Oil.—These very similar and remarkable oils are obtained from the soft fat of the head and jaw of two marine animals belonging to the family *Delphinidæ*, viz.:—the common porpoise, *Delphinus phocæna*, and the bottlenose dolphin, *Delphinus globiceps*. The fat is first washed in fresh water, then put into covered tins and heated for several hours in a closed digester with steam under the pressure of about 10 pounds per square inch. The tins are then opened, and the liberated oil is poured off from the coagulated membrane and washed with water. It is then exposed to a low temperature, and the portion which remains fluid is separated. This oil, carefully strained to remove all solid fat, is a straw-yellow, limpid liquid. It is specially prepared in the United States for lubricating watches and other delicate mechanism, and commands a very high price. Chemically, it consists largely of the glycerides of valeric and other volatile fatty acids of the acetic series.

'**Melon Oil**' derives its name from the shape of the mass of fat taken from the head of the dolphin, reaching from the spout-hole to the end of the nose, and from the top of the head to the upper jaw.

When taken off in one piece it has the shape of a half water-melon, weighs about 25 pounds, and yields about 6 quarts of oil.

Specimens of these oils, and of the crude oils from which they are obtained, have been examined by Moore,* with the following results:—

TABLE XXV.—PROPERTIES OF PORPOISE AND DOLPHIN JAW OILS.

	DESCRIPTION OF OIL.	Saponification Value %.	Hehner Value %.	Total Volatile Fatty Acids as Valeric Acid %.	Reichert Value, c.c. required by 2·5 grms.	Iodine Value %.
1	Porpoise jaw oil, skimmed and strained,	25·37	72·05	19·91	47·77	49·6
2	Porpoise jaw oil, skimmed and strained,	27·23	68·41	24·30	56·00	30·9
3	Dolphin jaw oil, skimmed and strained,	29·00	66·28	28·17	65·92	32·8
4	Porpoise jaw oil, unstrained,	14·39	96·50	1·64	2·08	76·8
5	Dolphin body oil, . .	19·73	93·07	2·71	5·60	99·5

A sample of porpoise jaw oil examined by Steinbuch had a Reichert-Meissl value of 131·6.

A sample labelled '*Superfine Watch Oil,*' manufactured by Ezra Kelley of New Bradford, Mass., obtained from a Derby watchmaker, had a pale golden-yellow colour, a sickly odour, and gave the following results:—

Sp. gr. at 60° F., 0·930.

Viscosity at 60° F. { Thicker than sperm oil. Comparative runnings from a 5 c.c. pipette showed the viscosity to be about 1·3 times that of sperm oil; = about 0·55 in absolute measure.

Reichert-Meissl value, 115·1.

Unsaponifiable matter, 10·6%. (Easily soluble in 90 per cent. alcohol, and resembling in appearance the wax alcohols of sperm oil.)

C.—BLOWN or THICKENED OILS.

These are fixed oils, usually rape or cottonseed, artificially thickened by a process of limited oxidation, which consists in forcing a current of air through the heated liquid. The oil, contained in a tall cylindrical iron vessel, is first raised to a temperature of about 170° F. by a steam-coil, air is then blown through it in streams of bubbles, at first cautiously to avoid too rapid a rise of temperature and frothing over of the contents of the vessel, afterwards more vigorously until the required viscosity is attained. Steam is shut off before commencing to blow air, as, by the process of oxidation, sufficient heat is evolved not only to maintain but to raise the temperature of the oil, and, in order to avoid too great a rise of temperature, provision should be made for passing, if necessary, a current of cold water through the steam-coil. Veitch Wilson states * that the temperature is usually allowed to rise to from 200° F. to 250° F., according to whether the quality of the product or the time occupied in the process is of the greater importance; the time may thus vary from 18 to 48 hours. Very irritating vapours, containing acetic and acrylic acids, are given off during the process, and are conveyed away by a pipe in the cover of the vessel.

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* *Jour. Amer. Chem. Soc.*, xi. (1889), p. 155.

Oils thus treated increase in density as well as in viscosity, and the blowing is continued until the desired specific gravity is attained. According to Veitch Wilson, the blown oils produced commercially for lubrication range in specific gravity from 0·955–0·960 at 60° F., with a viscosity at 180° F. equalling that of castor oil at 60° F., to 0·980–0·985 at 60° F., with a viscosity at 180° F. about four or five times greater than that of castor oil.

Blown oils are paler in colour than the oils from which they have been produced, and they have a characteristic nauseous odour. Though sparingly soluble in alcohol, they are somewhat more soluble than the untreated oils, and they readily dissolve in petroleum spirit. They do not mix with mineral lubricating oils in all proportions, a certain minimum amount (usually 20–30 per cent.) of blown oil being necessary to give a clear solution; this minimum is greater the lower the temperature, so that a mixture which is clear when warm may separate on cooling, and it varies according to the specific gravity and origin both of the mineral oil and of the blown oil.

The nature of the chemical changes which occur during the blowing process has been studied by Fox and Baynes † and Thomson and Ballantyne, ‡ but is not thoroughly understood. Glycerides of hydroxy acids are formed in considerable quantity (see p. 240), and the iodine value of the oil diminishes. Glycerides of insoluble fatty acids become largely converted into glycerides of soluble, chiefly non-volatile, acids, and the saponification value of the oil is increased. There is an increase of 1½ to 2 per cent. in the free fatty acids, but the percentage of unsaponifiable matter is not much changed. The evolution of heat in Maumené's test is also much increased. The results in Table XXVI. were obtained by Thomson and Ballantyne.

The blown oils chiefly produced for the manufacture of lubricants

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* Carpenter and Leask, *Soap, Candles, Lubricants, etc.*, pp. 268–272.

† *Analyst*, xii. (1887), p. 33.

‡ *Jour. Soc. Chem. Ind.*, xi. (1892), p. 506.

are blown rape oil, blown ravison oil, and blown cottonseed oil or 'lardine.' Cottonseed oil is the most easily thickened by blowing, but the product does not mix so freely with mineral oil as blown rape oil of the same density, and the latter oil generally appears to produce a better lubricant (*Veitch Wilson*).

Blown oils in admixture with mineral oils are very largely used as lubricants, and for certain purposes, such as the lubrication of marine engines, such mixtures appear to supply a distinct want. The mineral oils entering into their composition are usually those of moderate viscosity, such as American pale '903/7.' Whether such mixtures are as suitable for railway work as those produced by mixing mineral oils of greater viscosity, such as American pale '910/20,' pale '912/15,' or dark (reduced) machinery oils, with untreated vegetable or

TABLE XXVI.—CHEMICAL CHANGES PRODUCED BY BLOWING.

Chemical and Physical Data.	No. 1. Pure Rape Oil.	No. 2. Partially Blown Rape Oil prepared from No. 1.	No. 3. Blown Rape Oil prepared from No. 1.	No. 4. Commercial Blown Rape Oil.	No. 5. Commercial Blown Cotton Seed Oil 'Lardine.'	No. 6. Pure Sperm Oil.	No. 7. Blown Sperm Oil prepared from No. 6.
Sp. gr. at 60° F. (15·5° C.)	0·9141	0·9275	0·9615	0·9672	0·9740	0·8799	0·8989
Free (oleic) acid, %	5·10	5·01	7·09	4·93	3·38	1·97	3·27
Saponification value, %	17·39	18·30	19·49	19·77	21·32	13·04	14·23
Insoluble acids (Hehner value), %	94·76	...	85·94	82·40	84·97	...	...
Soluble non-volatile acids, %	0·52	...	9·20	11·16	9·00	...	...
Soluble volatile acids, %		...	0·82	1·90	1·94	...	...
Iodine value, %	100·5	88·4	63·2	63 6	56·4	82·1	67·1
Specific temperature reaction,	135	...	...	253	227	...	...
Unsaponifiable matter, %	0·65	...	0·76	2·80	1·00	36·32	34·65
Fatty Acids.							
Iodine value of insoluble acids,	...	...	66·5	70·2	62·7	...	...
Molecular weight of insoluble acids,	...	...	327	317	296	...	...
Molecular weight of soluble non-volatile acids,	...	...	241	...	...	...	...
Molecular weight of soluble volatile acids,	...	...	72	76	104	...	...

animal oils such as rape or tallow oil, is a question which needs careful investigation. So experienced an authority as Mr. Veitch Wilson, who is a manufacturer of these oils, points out* that although mixtures containing blown oils have been used for several years without serious complaint, "it appears to be an anomaly that oils of well-known oxidizing tendency like those from cotton seed or rape seed should, after having their gumming and drying tendencies developed by blowing, be adopted as the basis for the production of lubricants; and the writer fears that, unless great care be exercised in removing superfluous oil from bearings on which such oil is used, the slow elimination of the mineral oil by evaporation will produce troublesome deposits on the machinery."

Although blown oils for lubricating are chiefly prepared from rape and cottonseed oils, the following have also been thickened by the blowing process, viz. :—olive, lard, earthnut, castor, maize, seal and sperm oils.

D.—ROSIN OIL.

Rosin oil is the principal product of the destructive distillation of common resin ('rosin' or colophony). The distillation is conducted in cast-iron stills heated by a fire below. The charge of rosin varies from 3 to 10 tons. The first portion of the distillate, boiling between 80° and 250° C. (176° and 482° F.), and amounting to about 2½ to 5 per cent. of the weight of the rosin, is a very complex, limpid liquid, known as resin spirit, which is used for varnish making and for the adulteration of oil of turpentine. This is followed, at a temperature above 300° C. (572° F.), by the rosin oil, which, if the distillation be pushed to dryness, may amount to 85 per cent. of the total products. About 2½ per cent. of water containing a little acetic acid passes over during the distillation, and a considerable quantity of gas is given off, consisting of oxides of carbon and hydrocarbons of the ethylene series. A residue remains in the still, consisting of either pitch or coke, according to the stage at which the distillation is arrested.

Crude rosin oil is a viscid liquid of more or less dark brown colour with a strong, usually blue or violet, fluorescence. It always contains a considerable proportion of rosin which has distilled over unchanged. By heating to a temperature of 150° C. (302° F.) for 3 to 4 hours, the last traces of spirit are removed, the oil loses from 1 to 5 per cent. in weight and acquires a green fluorescence. By well boiling with water to expel acetic acid and redistilling once or twice from caustic soda, refined rosin oils are obtained which are pale in colour. The fluorescence or bloom is destroyed by exposing the oil to the air and sunlight in shallow vessels, or by treatment with hydrogen peroxide, nitro-naphthalene, etc.

Commercial rosin oils usually range in specific gravity, according to Lewkowitsch, from about 0·96 to 0·99, but oils are met with having a specific gravity as high as 1·001. Rosin oils are strongly dextro-rotatory, the rotation varying from 30 to 40 degrees or more in a 100 mm. tube. These properties, the ready solubility of rosin oils in acetone, and certain colour reactions, are made use of to distinguish them from mineral oils (see p. 284).

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* Carpenter and Leask, *Soap, Candles, Lubricants, etc.*, p. 272.

Rosin oils when titrated with alcoholic potash neutralize an amount of alkali which varies according to the quantity of resin acids they contain. According to Leeds* the crude oils neutralize from 2·8 to 4·4 per cent. of potash (KOH), but by careful distillation or refining they can be obtained almost neutral. Esters or anhydrides are also present which do not neutralize alkali in the cold, but can be saponified by boiling with potash as in determining the saponification value (p. 211). The resin acids can be obtained from the soap solution gravimetrically by acidifying and shaking with ether, after removing the neutral rosin oil as described in Chap. VII., p. 215. Rosin oil has the property of combining with calcium hydroxide and other bases, forming peculiar greasy bodies. This property is utilized in the manufacture of [illegible] greases (see p. 124).

The chemical composition of rosin oil is not fully known. According to Renard† the neutral oil purified from acid substances by washing with caustic soda solution, consists to the extent of about 80 per cent. of [illegible] boiling at 343°–346° C. (649°–655°F.); about 10 per cent. is [illegible], and about 10 per cent. [illegible]. The hydrocarbon [illegible] obtained by Renard, when exposed to the air in thin layers for five days, absorbed about one-tenth of its weight of oxygen and dried to a varnish.

Rosin oil is [illegible] for batching jute. It is not suitable for the lubrication of machinery, but is used to adulterate mineral and other lubricating oils. The methods for its detection are given in the chapter following.

II.—LUBRICANTS CONTAINING SOAP. GREASES.

Soap-thickened Oils.—Mineral oils are sometimes artificially thickened by dissolving soap in them. Aluminium soap is usually employed for this purpose. It is prepared by saponifying whale, cotton-seed, or lard oil, or by neutralizing commercial oleic acid with caustic soda, and pouring the solution of soda soap gradually into a solution of common alum, stirring all the time. Crude aluminium oleate separates out as an insoluble, gummy precipitate, which is pressed free from water and heated with about 4 times its weight of mineral oil until dissolved. The gelatinous material thus produced is sold for thickening oils under the names '*viscom*,' '*oil-pulp*' or '[illegible],' '[illegible],' etc. A comparatively small quantity melted into a mineral oil will considerably increase its apparent viscosity.

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* *Jour. Soc. Chem. Ind.*, xi. (1892), p. 308.

† *Jour. Chem. Soc.*, 1888, Abs., p. 161.

Mineral oils thickened in this way can easily be recognised by the tendency to form threads when the oily cork is removed from the bottle, and by their peculiar non-homogeneous appearance, resembling a mixture of oil and jelly. The spurious viscosity rapidly diminishes when the oil is heated. Schweitzer regards this addition to mineral oils as pure adulteration, and states that experience has shown that in contact with water and steam the aluminium soap is precipitated and clogs the machinery. On the other hand, Bloede states that by the presence of aluminium soap the adherence of the lubricant to metal surfaces is much increased.

Aluminium soap is not exclusively used as a thickener. A sample of thickened oil analysed by Archbutt had the following composition:—

Russian mineral oil (0·909), ...	97·08
Neutral fatty oil, ...	·58
Fatty acids as soap, etc., ...	1·97
Ash, chiefly $CaCO_3$, ...	·12
	99·75

In this case, about 2 per cent. of lime soap was the thickener used. The Russian oil, freed from soap by washing with hydrochloric acid, had a viscosity at 60° F., about 3 times that of refined rape oil. The 2 per cent. of soap made it so viscid at 60° F. that it would not flow through the viscometer. The sample had the appearance of a non-homogeneous mixture of jelly and oil, and formed threads in dropping.

Soap-thickened Greases.—Under this name may be included the various greases which consist of mineral oil thickened with sufficient soap to form at ordinary temperatures a consistent grease. The soaps usually employed for this purpose are lime, soda, or lead soaps, made with various fats and oils. I. J. Redwood * has described in detail a process of manufacturing a grease of this kind from mineral oil, horse fat, and lime, from which the following is abbreviated.

The fat is melted in a steam-jacketed kettle provided with a mechanical stirrer, and is raised to a temperature of about 180° F. Cream of lime is then added in sufficient quantity to saponify the fat, the cover is put on, and the whole is boiled and stirred until saponification is complete and a little of the soap rubbed down in the palm of the hand exudes only a few minute drops of water. A portion of the mineral oil at a temperature of about 190° F. is then slowly sprayed on to the soap in the kettle, and is thoroughly incorporated with it by continual stirring; a further quantity of mineral oil is then sprayed in cold, until the desired consistency is reached. After continuing to stir for about ½ hour longer, the still hot contents of the kettle are run off through a cooling pipe into a grinding mill, in which all lumps are reduced and the grease is made of a uniform smooth consistency. It is then packed in casks.

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* *Lubricants, Oils, and Greases* (Spon).

[illegible] thickened with a [illegible] saponified [illegible] thickened with a [illegible] often [illegible] The [illegible] those [illegible] soda, [illegible] to cut [illegible] nitro-benzene, [illegible] mill for the purpose of [illegible] useful [illegible] These greases may [illegible] mere [illegible] The following are a few [illegible] —

[illegible] Soap Greases [illegible]

	[illegible]	[illegible]	[illegible]	4.	5.
Mineral oil [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	74·5
[illegible]	...	...	[illegible]	·5	·4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	17·6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1·5
Water, by difference,	[illegible]	[illegible]	[illegible]	[illegible]	6·1*
	[illegible]	[illegible]	[illegible]	[illegible]	100·1

* [illegible]

II. Soda Soap Greases.

	1.	2.
Mineral oil [illegible]	53·00	70·93
Neutral fat, [illegible]	8·97	2·02
Dry soda soap,	16·11	9·30
Sodium silicate,	...	6·10
Sodium carbonate,	3·19	...
Sodium sulphate,	1·67	...
Water, by difference,	15·06	11·65
	100·00	100·00

c. LEAD SOAP GREASE.

Mineral oil (0·900),	48·0
Neutral fat,	8·7
Fatty acids,	2·6
Resin acids,	9·9
Lead oxide,	3·0
Lime,	0·9
Water,	27·2
	100·3

Railway Wagon Grease.—The yellow grease used in the axle-boxes of railway wagons is composed usually of tallow, palm oil, soap, and water. Lant Carpenter states that a grease containing from 1·1 to 1·2 per cent. of soda has been found to give the best results. The tallow and palm oil are heated to 180° F. (82° C.), and a solution of the carbonate of soda in the water heated to 200° F. (93·5° C.) is allowed to flow into the melted oil; the whole is then well stirred together and run into large tubs to cool slowly. The following formulæ for greases of this kind are said to have stood the test of successful experiment.

TABLE XXVIII.—FORMULÆ FOR RAILWAY WAGON GREASE.

Materials.	Summer.	Medium.	Winter.
Tallow,	22·0	20·0	18·0
Palm oil,	12·0	12·0	12·0
Sperm or colza oil,	1·0	1·5	2·0
Soda crystals,	5·0	5·0	5·0
Water,	60·0	61·5	63·0
	100·0	100·0	100·0

The soda crystals (sodium carbonate) in the above formulæ would have the effect of neutralizing and forming a more or less perfect soap with the free fatty acids contained in the palm oil and tallow, but it would probably be better, instead of adding a fixed weight of sodium carbonate, to add sufficient caustic soda to neutralize the free acid actually present in the fat used.

Sometimes a manufactured soap made from palm oil is added; thus the grease formerly used on the Midland Railway was made by dissolving 6 cwt. of palm soap in twice its weight of water and adding to the soap solution 6 cwt. of tallow and 2 cwt. of palm oil. The well-stirred mixture was run into shallow iron pans in which it was stirred with wooden paddles until set. The palm oil is now replaced by a dark mineral oil, the process of manufacture remaining in other respects the same. The following is the percentage composition of this grease after allowing 2½ per cent. for loss by evaporation of water during manufacture:—

Tallow,	23·3
Palm oil or mineral oil,	7·8
Dry soap,	16·3
Water,	52·6
	100·0

In an experiment made on the Great Western Railway in 1865, under the direction of Mr. Clayton, now Carriage and Wagon Superintendent of the Midland Railway, a train of passenger carriages lubricated with axle-grease ran 4999 miles in four weeks without replenishing the axle-boxes, and at the end of that time about 66 lbs. of grease had been used. This quantity was equivalent to 21 ounces of grease per 100 miles for the whole train, or 3½ ounces for each carriage, or less than 1 ounce of grease per axle-box per 100 train miles.

Rosin Grease.—It has already been stated (p. 120) that rosin oil has the property of uniting with calcium hydroxide to form a grease.

Rosin grease is made by stirring rosin oil with about three-fourths of its weight of slaked lime made into a cream with water. The oil and lime rapidly unite, extruding the superfluous water, which is drained off, and the grease is diluted by gradually stirring in a further quantity of oil, until the desired consistency is attained. The oil used for diluting may be rosin oil, petroleum oil, or neutral coal-tar oil ('grease oil,' naphthalene oil). Barytes, gypsum, whiting, and other filling materials are also sometimes added.

I. J. Redwood describes the following method of making a '*set-*' or axle-grease from rosin oil and mineral oil:—Dry sifted slaked lime and twice its weight of mineral oil are thoroughly stirred together for several hours, until a perfectly uniform mixture is produced. A certain quantity of this prepared liquid, called the 'lime part,' is run into a barrel or other receptacle, and, whilst being vigorously stirred by means of a perforated metal disc attached to a handle, which is worked up and down in the barrel, the rosin oil or 'set' is quickly run in, and the whole is stirred for a few seconds and then allowed to remain at perfect rest until thoroughly set, which will take place in from 5 to 15 minutes.

Rosin greases are used to lubricate the iron axles of colliery trucks and ordinary road vehicles. They are not suitable for brass bearings, on account of the rapidity with which the grease *acetifies* under the influence of heat and friction.* The composition of rosin grease is shewn by the following analyses:—

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* Mills, *Destructive Distillation*, p. 98.

Hydrocarbon oil (0·954),	87·7
Resin,	3·7
Slaked lime ($Ca(OH)_2$),	6·4
Water, by difference,	2·2
	100·0

Hydrocarbon oil (0·962),	86·6
Resin,	7·0
Slaked lime ($Ca(OH)_2$),	4·5
Water, etc.,	1·9
	100·0

Screwing and Drilling Liquids.—The liquid used for lubricating cutting tools is usually a solution in water of soft soap and soda. The liquid used at one works is made by boiling in 100 gallons of water 18·5 pounds of soda and 15·5 pounds of soft soap. Another lubricant of this kind was found by analysis to be a solution of rosin soap in rosin oil. It had the following composition:—

Resin oil,	74·9
Resin acids,	23·5
Soda (Na_2O),	1·5
Oxide of iron and lime,	·1
	100·0

CHAPTER VI.

PHYSICAL PROPERTIES AND METHODS OF EXAMINATION OF LUBRICANTS.

A.—VISCOSITY AND VISCOMETRY.

THE meaning of viscosity having been explained and the subject discussed generally in Chapter II., the methods of measuring the viscosities of oils and other liquids (‘*viscometry*’) will alone be considered here. Various methods have been proposed, based upon such observations as the rate of ascent of air-bubbles or hollow glass spheres in the liquid*; the torsional vibration of a disc in its own plane when suspended by a wire and immersed in the liquid†; the speed of rotation of paddle wheels, cylinders, etc., immersed in the liquid and kept in motion by a falling weight,‡ etc., etc. None of these methods have proved satisfactory or come into general use. The most accurate, and the most generally employed method for exact work, is that of Poiseuille, in which the rate of flow of the liquid through a capillary tube under known conditions of temperature and pressure is measured; but for commercial purposes the comparative viscosities of lubricating oils are almost invariably ascertained by measuring and comparing the rates of discharge (‘efflux velocities’) of the oil and of some standard liquid from a small orifice or jet.

We shall commence with a description of the method of Poiseuille; for although that method has never come into general use for commercial purposes, it has occasionally been employed for a special purpose, and we have used it for determining the viscosities of mixtures of glycerol and water from which the table on pp. 134–137 was constructed.

Absolute Viscometry.

Determination of Viscosity in Absolute Measure.—Poiseuille's method of viscometry depends upon the following facts, which he proved experimentally:—(1), that the rate of flow of liquid through a capillary tube of suitable dimensions is proportional to the pressure, and inversely proportional to the length of the tube, and (2), that the rate of flow through a capillary tube of cylindrical bore is proportional to the fourth power of the radius of the bore. Prof. Osborne Reynolds has shown* that to ensure these conditions of steady viscous flow the proportions of the tube must be such that $\frac{r_0 \bar{v} d}{\eta}$ is less than 700, where r_0 is the radius of the bore, $\bar{v}$ the mean velocity of the fluid, d the density of the fluid, and η its viscosity. The viscosity of the fluid in absolute measure is then given, approximately, by Poiseuille's formula,

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* Mills. See Redwood, *Petroleum*, vol. ii. p. 619.

† Doolittle, *Jour. Amer. Chem. Soc.*, xv. (1893), p. 173; and *Jour. Soc. Chem. Ind.*, xii. (1893), p. 709.

‡ Napier and Cockrell. See Redwood, *Petroleum*, vol. ii. p. 619.

$$\eta = \frac{\pi g d h r_0{}^4 t}{8 V a},$$

in which g is the acceleration due to gravity, d the density of the fluid, h the mean head, t the time, V the volume of liquid discharged, and a the length of the tube.

To obtain the true viscosity, corrections must be made: (α) for the viscous resistance to the flow of the liquid at the ends of the tube; (β) for the abnormal flow of the liquid on first entering the tube; (γ) for the kinetic energy with which the liquid leaves the tube; and (δ) for the resistance due to surface tension effects at the discharge orifice. Corrections α and β have never yet been devised, but errors due to these effects may be reduced to very small proportions by making the tube long. Correction γ is made by deducting from the mean head a quantity $= \frac{v^2}{g}$; this correction may be made very small by using a tube so narrow and so long that the movement of the liquid is very slow. The error due to surface tension effects, which may be serious, is so variable that the correction δ is best eliminated altogether by immersing the discharge orifice in the liquid and making a suitable deduction from the head.

Description of an Absolute Viscometer.—The apparatus employed by the authors is illustrated in fig. 35. The capillary tube A was carefully selected and calibrated from end to end, and was found to be of practically uniform bore. Viewed through a lens magnifying 20 diameters, the bore appeared to be perfectly cylindrical in section. The diameter, calculated from the weight of mercury required to fill the tube, was 0·6180 mm., and the length of the tube, measured by a Whitworth machine, was 21·991 cm. Thus the length was about 350 times the diameter, and, as we estimate from experiments made with Redwood's viscometer that the magnitude of the correction α (see above) is about equal to the friction of a length of capillary tube equal to the diameter of the bore, our results from this cause cannot be more than about 0·28 per cent. too high. The kinetic energy correction, γ, also became very small, owing to the narrowness of the bore, amounting to only 0·5 per cent. of the head in the case of water (viscosity $=$ 0·01), and, being quite negligible in the case of all the glycerol solutions except the thinnest ($\eta = 0·0379$), and in that making a difference of only 0·05 per cent., or 2 in the fifth decimal place.

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* See Chap. II.

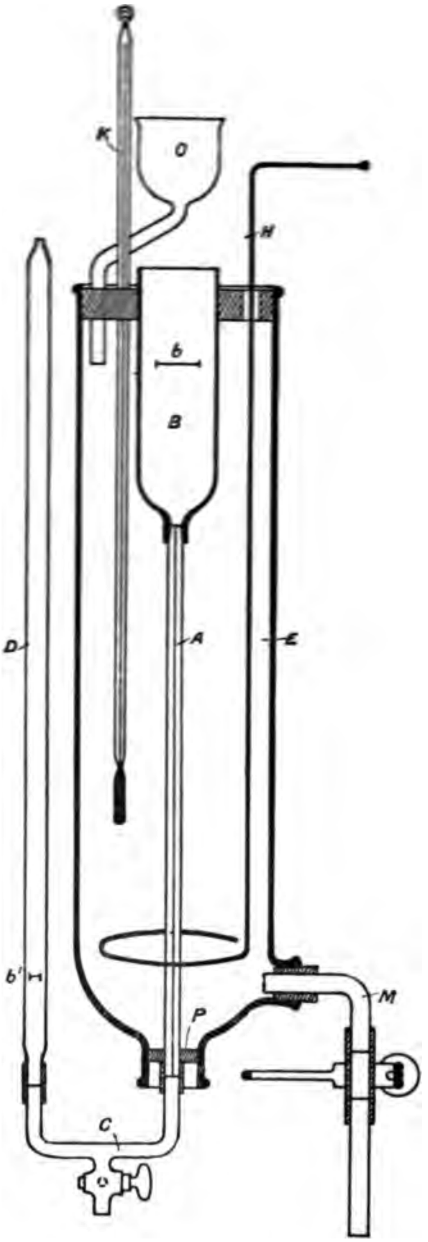

FIG. 35.—ABSOLUTE VISCOMETER.

The capillary tube was ground into the neck of the reservoir B, and was connected at its lower end, through the wide glass tube C, with the measuring tube D. The glass water-jacket E for maintaining the temperature constant contained a stirrer of brass wire H and a thermometer K, indicating tenths of a degree centigrade. By drawing off a little water through the tube M, and adding either warmer or colder water through the funnel tube O, and vigorously stirring, the slightest alteration in the temperature of the bath could be corrected at once. This is a most important point, for the viscosity even of water undergoes a remarkably rapid alteration with change of temperature. Thus, the viscosity of water, which is about 0·013 at 10° C., falls to 0·010 at 20° C., or an average diminution of 2·3 per cent. per degree. The viscosity of oils, especially mineral oils, and of many other liquids, changes at a much greater rate. Bearing in mind the great importance of keeping the temperature of the liquid constant, the india-rubber disc P, closing the lower neck of the waterjacket, was made only about $\frac{3}{16}$ inch thick and was pushed high up into the neck in order that the projecting end of the capillary tube below the water-line should be as short as possible, and well screened from currents of cooler or warmer air. The tubes C and D, which were not part of the original design of the apparatus, were added in consequence of the erratic results caused by the varying tension of the free surface of the liquid (correction δ), when the end of the capillary tube was open to the air. D was drawn out to a point at the upper end, in order to prevent, or reduce to a minimum, evaporation of, or absorption of moisture from the air by, the liquid in the tube. D was not jacketed; but as all our experiments with this apparatus were made at 20° C., which was very nearly the temperature of the laboratory, any error due to the very slight difference in the temperature, and therefore in the density, of the fluid in D as compared with that in B, must have been quite negligible. The tube D was carefully calibrated, and the capacity in c.c. per millimetre, from the zero mark *b′* upwards, was accurately ascertained. The reservoir B was also calibrated, from the zero mark *b* downwards. The vertical distance between the two zero marks, measured by a cathetometer, was 25·50 cm. The shaded portions of the figure represent indiarubber connections.

Method of Experiment.—The tube C was first of all disconnected from tubes A and D, and each was thoroughly well washed with water, then rinsed with alcohol and ether, and dried by aspirating air through it. Having filled B, A, and C, and moistened the inner surface of D with the liquid to be tested, C was again fixed in position, taking care that no air bubbles were entrapped, and that the ends of the tube were pushed into close contact with the ends of A and D. The height of D was then adjusted in the clamp holding it, so that the zero mark *b′* was exactly level with a fixed mark on the capillary tube A. The upper end of the capillary tube was closed, meanwhile, by a valve made of a small cork fixed on the end of a platinum wire. The liquid was allowed to remain at rest until the temperature had settled down to exactly 20° C., and during this time the free surfaces of the liquid in B and D were accurately adjusted to the zero marks. All being ready, and the liquid perfectly motionless, the cork valve was raised and the liquid allowed to flow; the time was then measured which the meniscus in D took to rise between two points, the heights of which above *b′* were successively measured by a cathetometer. In experimenting with a thin liquid like water, the fluid rose in D with comparative rapidity, and after each experiment the valve was closed and the liquid readjusted to the zero marks; but with the glycerin solutions the rise took place so slowly that several successive observations could be taken without stopping the flow of liquid. The excess of tension of the meniscus in the narrow tube D over that in the wide tube B was ascertained separately for each liquid by connecting D with a tube of the same diameter as B, without the intermediate capillary tube, and measuring with the cathetometer the difference in height of the liquid columns which balanced each other in the two tubes; this difference was added to the measured head.

The apparatus, as shown in fig. 35, was found to give very good results with liquids whose viscosity did not exceed that of rape oil (about 1·11 at 60° F.). With more viscous fluids, the movement was so sluggish that it was found necessary to increase the pressure by lowering the tubes C and D and inserting a connecting tube between C and A. In these experiments, the head was measured by the cathetometer on a millimetre scale suspended vertically by the side of the apparatus.

Experimental Determination of the Viscosity of Water at 20° C.—This determination was made to test the capabilities of the apparatus and method of working. The distilled water used was well boiled in a silver flask to expel dissolved gases, cooled to 20° C., and immediately introduced into the viscometer.

t, the mean time of flow, was measured by a stop-watch which was started and stopped as the meniscus in D passed two points, 2·155 cm. and 10·83 cm. respectively, above zero (*b′*). Five experiments were made, and the times recorded were 136·2, 136·3, 135·8, 135·9, and 135·8 seconds; hence the mean time was *136·0 seconds.*

V, the volume of water flowing through the capillary tube in t seconds, was the capacity of D between the two points above referred to, and amounted to *4·00756 c.c.*

h, the mean head of water, was calculated by subtracting from the vertical distance bb', the initial and final distances of the liquid surfaces below b and above b', one centimetre of tube D being equal in capacity to 0·032 centimetre of B. Thus:—

	Centimetres.
Initial head = 25·50 − 2·155 − (2·155 × 0·032)	= 23·28
Final head = 25·50 − 10·83 − (10·83 × 0·032)	= 14·32
Mean	= 18·80
Add excess tension of meniscus in D	·28
Mean head (h)	= 19·08
Subtract for kinetic energy of efflux (h^1) $\frac{v^2}{g}$, where $v = \frac{V}{\pi r_0^2 t}$, (*Wilberforce*)	= ·098
Corrected mean head ($h - h^1$)	= 18·982 cm.

d, the density of water at $\frac{20^\circ}{4^\circ}$ C., = 0·998259

r_0, the radius of the capillary tube, = 0·0309 cm.

a, the length of the capillary tube, = 21·991 cm.

g, the acceleration due to gravity, = 980·51 cm. seconds.

π, = 3·14159

Then, by the formula (*Poiseuille-Wilberforce*)

$$\eta = \frac{\pi r_0^4 t g d (h - h^1)}{8Va} = 0·01028.$$

Therefore, the absolute viscosity of water in C.G.S. units at 20° C. determined by this apparatus is 0·01028 dyne per sq. cm.*

Viscosities at 20° C. of Mixtures of Glycerol and Water.—The glycerin used for these determinations was purchased as pure from Messrs. Hopkin & Williams. The specific gravity at $\frac{20^\circ}{20^\circ}$ C. was 1·2568, corresponding to 98 per cent. of glycerol and 2 per cent. of water according to Gerlach's table. The viscosity of this was carefully determined, without dilution. It was then mixed with distilled water. Six different mixtures were prepared, having a suitable range of viscosities, and the specific gravity and viscosity of each mixture were carefully determined. The data and results obtained are given in the following tables.

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* Magnus Maclean (*Physical Units*, 1896) gives the value 0·0102, based upon results obtained by Sprung (1876), Meyer (1877), and Slotte (1883). Thorpe and Rodger (*Phil. Trans.*, vol. clxxxv. A, p. 397) obtained the value 0·010015, and have recalculated the values obtained by previous observers with the following results:—Poiseuille, 0·01008; Sprung, 0·01003; Slotte, 0·01008.

TABLE XXIX.—VISCOSITIES IN DYNES PER SQ. CM. OF MIXTURES OF GLYCEROL AND WATER.

GLYCERIN No. 1.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·1007

" " $\frac{20^\circ}{4^\circ}$ 1·0988

Glycerol = 40·0 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1	0·9298	22·51	89·3	0·0379
2	1·3809	17·87	167·8	0·0381
3	2·7868	21·48	278·7	0·0377
4	3·7052	20·45	390·1	0·0378

GLYCERIN No. 2.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·1848

" " $\frac{20^\circ}{4^\circ}$ 1·1828

Glycerol = 71·04 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1	0·9297	22·75	511·6	0·2364
2	0·9298	20·17	574·1	0·2351
3	0·9188	17·59	654·2	0·2365

GLYCERIN No. 3.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·2057

" " $\frac{20^\circ}{4^\circ}$ 1·2037

Glycerol = 78·78 % (*Gerlach*).

Number of Experiment.		Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1st *Series.*	1	0·4647	23·47	518·2	0·5029
	2	0·4651	21·92	549·1	0·4972
	3	0·4652	20·37	579·4	0·4875
2nd *Series.*	4	0·6975	22·03	817·6	0·4962
	5	0·6973	19·97	905·3	0·4982
	6	0·6895	17·91	1014·2	0·5062

TABLE XXIX.—*continued.*

GLYCERIN No. 4.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·2155

" " $\frac{20^\circ}{4^\circ}$ 1·2134

Glycerol = 82·41 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (*h*) cm.	Time (*t*) Seconds.	Viscosity (η).
1	0·4644	24·61	729·3	0·7486
2	0·6971	23·22	1165·6	0·7520
3	0·6977	21·36	1262·5	0·7486

GLYCERIN No. 5.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·2240

" " $\frac{20^\circ}{4^\circ}$ 1·2218

Glycerol = 85·55 % (*Gerlach*).

	Number of Experiment.	Volume (V) c.c.	Mean Head (*h*) cm.	Time (*t*) Seconds.	Viscosity (η).
1st Series.	1	0·4645	24·12	1099·9	1·1142
	2	0·6973	22·62	1742·0	1·1024
2nd Series.	3	0·4649	22·26	1193·0	1·1144
	4	0·4652	21·02	1258·0	1·1089
	5	0·4646	19·77	1345·0	1·1166

GLYCERIN No. 6.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·2463

" " $\frac{20^\circ}{4^\circ}$ 1·2441

Glycerol = 93·96 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (*h*) cm.	Time (*t*) Seconds.	Viscosity (η).
1	0·4645	98·63	969	4·0861
2	0·4649	97·19	980	4·0687
3	0·4652	95·43	1001	4·0779
4	0·4640	93·99	1015	4·0832

TABLE XXIX.—*continued.*

GLYCERIN No. 7.—Specific Gravity at $\frac{20^\circ}{20^\circ}$ 1·2568

" " $\frac{20^\circ}{4^\circ}$ 1·2546

Glycerol = 98·0 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (*h*) cm.	Time (*t*) Seconds.	Viscosity (η).
1	0·4644	99·25	2030	8·6884
2	0·4648	97·70	2051	8·6337
3	0·4650	96·46	2103	8·7366

COLLECTED RESULTS AND MEAN VALUES.

GLYCEROL AND WATER.—Viscosity at 20° C.							
Sp. gr. at $\frac{20^\circ}{20^\circ}$	1·1007	1·1848	1·2057	1·2155	1·2240	1·2463	1·2568
" " $\frac{20^\circ}{4^\circ}$	1·0988	1·1828	1·2037	1·2134	1·2218	1·2441	1·2546
Glycerol % (*Gerlach*)	40·0	71·04	78·78	82·41	85·55	93·96	98·0
η	0·0379	0·2364	0·5029	0·7486	1·1142	4·0861	8·6884
	0·0381	0·2351	0·4972	0·7520	1·1024	4·0687	8·6337
	0·0377	0·2365	0·4875	0·7486	1·1144	4·0779	8·7366
	0·0378	...	0·4962	...	1·1089	4·0832	...
	...	...	0·4982	...	1·1166	...	...
	...	...	0·5062	...	...	...	...
Mean values of η	0·0379	0·2360	0·4980	0·7497	1·1113	4·0790	8·6862

The logarithms of the mean values of η in the above table of collected results were plotted upon a diagram as ordinates, and the specific gravities at $\frac{20^\circ}{20^\circ}$ as abscissæ. It was found that a very regular curve could be drawn through the seven points, confirming the general accuracy of the results. By means of this curve the lengths of the ordinates corresponding to specific gravities ranging from 1·00 to 1·262 were carefully measured and gave the values of the corresponding logs. of η to three decimal places. On tabulating these logs. it was found that the increment was not quite regular, owing to the unavoidable irregularity of the curve as drawn. A systematic correction was therefore made which, while not altering the values of the logs. beyond the possible errors of experiment, made the increment a regular one. The corrected logs. thus obtained are given in Table XXX., with the corresponding viscosities to four figures.*

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER.

Sp. Gr. at $\frac{20}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20^\circ}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·000	·01028	$\bar{2}$·01183		1·032	·01513	$\bar{2}$·17992	532
1·001	·01040	$\bar{2}$·01703	520	1·033	·01532	$\bar{2}$·18525	533
1·002	·01053	$\bar{2}$·02223	520	1·034	·01551	$\bar{2}$·19058	533
1·003	·01065	$\bar{2}$·02744	521	1·035	·01570	$\bar{2}$·19592	534
1·004	·01078	$\bar{2}$·03265	521	1·036	·01590	$\bar{2}$·20127	535
1·005	·01091	$\bar{2}$·03786	521	1·037	·01609	$\bar{2}$·20663	536
1·006	·01104	$\bar{2}$·04307	521	1·038	·01629	$\bar{2}$·21200	537
1·007	·01118	$\bar{2}$·04829	522	1·039	·01650	$\bar{2}$·21738	538
1·008	·01131	$\bar{2}$·05351	522	1·040	·01670	$\bar{2}$·22277	539
1·009	·01145	$\bar{2}$·05873	522	1·041	·01691	$\bar{2}$·22817	540
1·010	·01159	$\bar{2}$·06395	522	1·042	·01712	$\bar{2}$·23358	541
1·011	·01173	$\bar{2}$·06918	523	1·043	·01734	$\bar{2}$·23900	542
1·012	·01187	$\bar{2}$·07441	523	1·044	·01756	$\bar{2}$·24443	543
1·013	·01201	$\bar{2}$·07964	523	1·045	·01778	$\bar{2}$·24987	544
1·014	·01216	$\bar{2}$·08488	524	1·046	·01800	$\bar{2}$·25532	545
1·015	·01231	$\bar{2}$·09012	524	1·047	·01823	$\bar{2}$·26078	546
1·016	·01246	$\bar{2}$·09536	524	1·048	·01846	$\bar{2}$·26625	547
1·017	·01261	$\bar{2}$·10061	525	1·049	·01870	$\bar{2}$·27173	548
1·018	·01276	$\bar{2}$·10586	525	1·050	·01893	$\bar{2}$·27722	549
1·019	·01292	$\bar{2}$·11112	526	1·051	·01917	$\bar{2}$·28272	550
1·020	·01307	$\bar{2}$·11638	526	1·052	·01942	$\bar{2}$·28823	551
1·021	·01323	$\bar{2}$·12165	527	1·053	·01967	$\bar{2}$·29375	552
1·022	·01339	$\bar{2}$·12692	527	1·054	·01992	$\bar{2}$·29928	553
1·023	·01356	$\bar{2}$·13220	528	1·055	·02018	$\bar{2}$·30482	554
1·024	·01372	$\bar{2}$·13748	528	1·056	·02044	$\bar{2}$·31037	555
1·025	·01389	$\bar{2}$·14277	529	1·057	·02070	$\bar{2}$·31593	556
1·026	·01406	$\bar{2}$·14806	529	1·058	·02097	$\bar{2}$·32150	557
1·027	·01424	$\bar{2}$·15336	530	1·059	·02124	$\bar{2}$·32708	558
1·028	·01441	$\bar{2}$·15866	530	1·060	·02151	$\bar{2}$·33267	559
1·029	·01459	$\bar{2}$·16397	531	1·061	·02179	$\bar{2}$·33827	560
1·030	·01477	$\bar{2}$·16928	531	1·062	·02207	$\bar{2}$·34389	562
1·031	·01495	$\bar{2}$·17460	532	1·063	·02236	$\bar{2}$·34953	564

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* Schöttner (*Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien*, vol. lxxvii. (1878), p. 682 ; and vol. lxxix. (1879), found the viscosity of pure glycerol at 20° C. = 8·304, but as he states the specific gravity at 20° C. = 1·2516 the correctness of his result is open to question. Schöttner's figures for dilute glycerin do not fall on any regular curve, and we have been unable to make any use of them.

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER—*continued.*

Sp. Gr. at $\frac{20^\circ}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20^\circ}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·064	·02266	$\bar{2}$·35519	566	1·109	·04302	$\bar{2}$·63369	684
1·065	·02296	$\bar{2}$·36087	568	1·110	·04371	$\bar{2}$·64057	688
1·066	·02326	$\bar{2}$·36657	570	1·111	·04441	$\bar{2}$·64749	692
1·067	·02357	$\bar{2}$·37229	572	1·112	·04513	$\bar{2}$·65445	696
1·068	·02388	$\bar{2}$·37803	574	1·113	·04586	$\bar{2}$·66146	701
1·069	·02420	$\bar{2}$·38379	576	1·114	·04662	$\bar{2}$·66852	706
1·070	·02452	$\bar{2}$·38957	578	1·115	·04738	$\bar{2}$·67563	711
1·071	·02485	$\bar{2}$·39537	580	1·116	·04817	$\bar{2}$·68279	716
1·072	·02519	$\bar{2}$·40119	582	1·117	·04898	$\bar{2}$·69000	721
1·073	·02553	$\bar{2}$·40703	584	1·118	·04980	$\bar{2}$·69726	726
1·074	·02588	$\bar{2}$·41289	586	1·119	·05065	$\bar{2}$·70457	731
1·075	·02623	$\bar{2}$·41877	588	1·120	·05152	$\bar{2}$·71193	736
1·076	·02659	$\bar{2}$·42467	590	1·121	·05240	$\bar{2}$·71935	742
1·077	·02695	$\bar{2}$·43059	592	1·122	·05331	$\bar{2}$·72683	748
1·078	·02732	$\bar{2}$·43653	594	1·123	·05425	$\bar{2}$·73437	754
1·079	·02770	$\bar{2}$·44249	596	1·124	·05520	$\bar{2}$·74197	760
1·080	·02809	$\bar{2}$·44847	598	1·125	·05619	$\bar{2}$·74963	766
1·081	·02848	$\bar{2}$·45447	600	1·126	·05719	$\bar{2}$·75735	772
1·082	·02887	$\bar{2}$·46049	602	1·127	·05823	$\bar{2}$·76513	778
1·083	·02928	$\bar{2}$·46653	604	1·128	·05929	$\bar{2}$·77298	785
1·084	·02969	$\bar{2}$·47259	606	1·129	·06038	$\bar{2}$·78090	792
1·085	·03011	$\bar{2}$·47867	608	1·130	·06150	$\bar{2}$·78889	799
1·086	·03053	$\bar{2}$·48478	611	1·131	·06265	$\bar{2}$·79695	806
1·087	·03097	$\bar{2}$·49092	614	1·132	·06384	$\bar{2}$·80508	813
1·088	·03141	$\bar{2}$·49709	617	1·133	·06506	$\bar{2}$·81328	820
1·089	·03186	$\bar{2}$·50329	620	1·134	·06631	$\bar{2}$·82156	828
1·090	·03232	$\bar{2}$·50952	623	1·135	·06760	$\bar{2}$·82992	836
1·091	·03279	$\bar{2}$·51578	626	1·136	·06892	$\bar{2}$·83836	844
1·092	·03327	$\bar{2}$·52207	629	1·137	·07029	$\bar{2}$·84688	852
1·093	·03376	$\bar{2}$·52839	632	1·138	·07169	$\bar{2}$·85548	860
1·094	·03426	$\bar{2}$·53474	635	1·139	·07314	$\bar{2}$·86416	868
1·095	·03476	$\bar{2}$·54112	638	1·140	·07463	$\bar{2}$·87292	876
1·096	·03528	$\bar{2}$·54753	641	1·141	·07617	$\bar{2}$·88177	885
1·097	·03581	$\bar{2}$·55397	644	1·142	·07775	$\bar{2}$·89071	894
1·098	·03635	$\bar{2}$·56044	647	1·143	·07939	$\bar{2}$·89974	903
1·099	·03689	$\bar{2}$·56694	650	1·144	·08107	$\bar{2}$·90886	912
1·100	·03745	$\bar{2}$·57347	653	1·145	·08281	$\bar{2}$·91807	921
1·101	·03802	$\bar{2}$·58003	656	1·146	·08460	$\bar{2}$·92737	930
1·102	·03860	$\bar{2}$·58662	659	1·147	·08645	$\bar{2}$·93676	939
1·103	·03920	$\bar{2}$·59324	662	1·148	·08836	$\bar{2}$·94625	949
1·104	·03980	$\bar{2}$·59989	665	1·149	·09033	$\bar{2}$·95584	959
1·105	·04042	$\bar{2}$·60657	668	1·150	·09237	$\bar{2}$·96553	969
1·106	·04105	$\bar{2}$·61329	672	1·151	·09448	$\bar{2}$·97532	979
1·107	·04169	$\bar{2}$·62005	676	1·152	·09665	$\bar{2}$·98521	989
1·108	·04235	$\bar{2}$·62685	680	1·153	·09890	$\bar{2}$·99520	999

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER—*continued.*

Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·154	·1012	$\bar{1}$·00529	1009	1·199	·3856	$\bar{1}$·58608	1600
1·155	·1036	$\bar{1}$·01548	1019	1·200	·4002	$\bar{1}$·60224	1616
1·156	·1061	$\bar{1}$·02578	1030	1·201	·4155	$\bar{1}$·61857	1633
1·157	·1087	$\bar{1}$·03619	1041	1·202	·4316	$\bar{1}$·63507	1650
1·158	·1114	$\bar{1}$·04671	1052	1·203	·4485	$\bar{1}$·65174	1667
1·159	·1141	$\bar{1}$·05734	1063	1·204	·4662	$\bar{1}$·66858	1684
1·160	·1170	$\bar{1}$·06808	1074	1·205	·4848	$\bar{1}$·68559	1701
1·161	·1199	$\bar{1}$·07893	1085	1·206	·5044	$\bar{1}$·70277	1718
1·162	·1230	$\bar{1}$·08989	1096	1·207	·5250	$\bar{1}$·72013	1736
1·163	·1262	$\bar{1}$·10096	1107	1·208	·5466	$\bar{1}$·73767	1754
1·164	·1295	$\bar{1}$·11215	1119	1·209	·5694	$\bar{1}$·75539	1772
1·165	·1329	$\bar{1}$·12346	1131	1·210	·5933	$\bar{1}$·77330	1791
1·166	·1364	$\bar{1}$·13489	1143	1·211	·6186	$\bar{1}$·79140	1810
1·167	·1401	$\bar{1}$·14644	1155	1·212	·6452	$\bar{1}$·80969	1829
1·168	·1439	$\bar{1}$·15811	1167	1·213	·6733	$\bar{1}$·82818	1849
1·169	·1479	$\bar{1}$·16990	1179	1·214	·7029	$\bar{1}$·84687	1869
1·170	·1520	$\bar{1}$·18181	1191	1·215	·7341	$\bar{1}$·86577	1890
1·171	·1563	$\bar{1}$·19384	1203	1·216	·7672	$\bar{1}$·88488	1911
1·172	·1607	$\bar{1}$·20600	1216	1·217	·8021	$\bar{1}$·90421	1933
1·173	·1653	$\bar{1}$·21829	1229	1·218	·8390	$\bar{1}$·92376	1955
1·174	·1701	$\bar{1}$·23071	1242	1·219	·8781	$\bar{1}$·94354	1978
1·175	·1751	$\bar{1}$·24326	1255	1·220	·9195	$\bar{1}$·96356	2002
1·176	·1803	$\bar{1}$·25594	1268	1·221	·9635	$\bar{1}$·98383	2027
1·177	·1857	$\bar{1}$·26875	1281	1·222	1·010	·00436	2053
1·178	·1913	$\bar{1}$·28169	1294	1·223	1·060	·02516	2080
1·179	·1971	$\bar{1}$·29476	1307	1·224	1·112	·04624	2108
1·180	·2032	$\bar{1}$·30796	1320	1·225	1·168	·06761	2137
1·181	·2096	$\bar{1}$·32130	1334	1·226	1·228	·08928	2167
1·182	·2162	$\bar{1}$·33478	1348	1·227	1·292	·11126	2198
1·183	·2231	$\bar{1}$·34840	1362	1·228	1·360	·13356	2230
1·184	·2302	$\bar{1}$·36216	1376	1·229	1·433	·15619	2263
1·185	·2377	$\bar{1}$·37606	1390	1·230	1·511	·17916	2297
1·186	·2455	$\bar{1}$·39010	1404	1·231	1·594	·20248	2332
1·187	·2537	$\bar{1}$·40428	1418	1·232	1·683	·22616	2368
1·188	·2622	$\bar{1}$·41860	1432	1·233	1·779	·25021	2405
1·189	·2711	$\bar{1}$·43307	1447	1·234	1·882	·27464	2443
1·190	·2803	$\bar{1}$·44769	1462	1·235	1·993	·29946	2482
1·191	·2900	$\bar{1}$·46246	1477	1·236	2·112	·32468	2522
1·192	·3002	$\bar{1}$·47738	1492	1·237	2·240	·35031	2563
1·193	·3108	$\bar{1}$·49245	1507	1·238	2·379	·37636	2605
1·194	·3219	$\bar{1}$·50767	1522	1·239	2·528	·40284	2648
1·195	·3335	$\bar{1}$·52304	1537	1·240	2·690	·42976	2692
1·196	·3456	$\bar{1}$·53856	1552	1·241	2·865	·45711	2735
1·197	·3583	$\bar{1}$·55424	1568	1·242	3·054	·48488	2777
1·198	·3716	$\bar{1}$·57008	1584	1·243	3·259	·51306	2818

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER—*concluded.*

Sp. Gr. at $\frac{20^\circ}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20^\circ}{20^\circ}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·244	3·481	·54164	2858	1·254	7·043	·84778	3218
1·245	3·721	·57061	2897	1·255	7·591	·88029	3251
1·246	3·981	·59996	2935	1·256	8·187	·91313	3284
1·247	4·263	·62969	2973	1·257	8·837	·94630	3317
1·248	4·569	·65979	3010	1·258	9·546	·97980	3350
1·249	4·901	·69025	3046	1·259	10·32	1·01363	3383
1·250	5·261	·72107	3082	1·260	11·16	1·04779	3416
1·251	5·653	·75224	3117	1·261	12·09	1·08228	3449
1·252	6·078	·78375	3151	1·262	13·10	1·11710	3482
1·253	6·540	·81560	3185				

Commercial Viscometry.

A very rough idea of the relative viscosity of an oil may be formed by shaking it in a bottle and observing the rate at which air-bubbles rise in the oil; the more sluggish the movement of equal-sized bubbles, the greater the viscosity of the oil.

A rough quantitative method is to fill a 10 c.c. pipette with the oil, fix it in a vertical position in a clamp and count the number of seconds occupied by the oil in flowing from a mark on the upper stem to another mark on the lower stem. Then clean the pipette with ether, dry it, and make another similar experiment with some standard oil, say rape. For the results to be at all comparable the oils must be at the same temperature when the experiment is made. To ensure this, small beakers containing 20 to 30 c.c. of each oil should be allowed to stand on a table side by side for an hour before making the test; the pipette may then be filled from each beaker in succession. As a rough test, for sorting quickly a number of samples of oil, this is useful.

For accurate work, a properly constructed viscometer must be employed. Those mostly used for practical laboratory work have very short efflux tubes of comparatively wide bore. From these instruments a running can be made in a short space of time, and the parts are easily cleaned and kept in order. But the rate of efflux is far from being proportional to the viscosity of very fluid liquids and water, though in the case of lubricating oils having a viscosity at least as great as that of sperm oil at 60° F. (0·42), the error does not exceed about 2 per cent. The best known instruments of this class are Redwood's, which is the standard instrument in this country, Engler's and Kunkler's which are used on the Continent, and viscometers used in the United States. There are many others, but we do not think it necessary to describe them all. The glass viscometer devised by Coleman and improved by Archbutt is one of the most [illegible] for [illegible] purposes. It will be described as the Coleman-Archbutt viscometer.

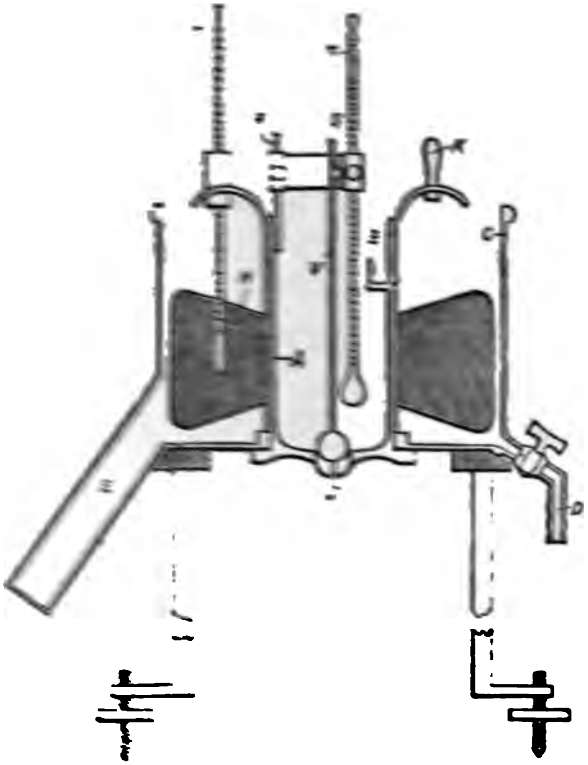

Fig. 85.

Redwood's Standard Viscometer.—*Construction.*—This instrument, fig. 85, consists of a silvered copper cylinder A, about 1¾ inches in internal diameter and 3½ inches deep, having a thick metal bottom, slightly concave on the inside, in the centre of which the agate jet J is fixed. In the instrument used by the authors the passage drilled through the jet is 12 millimetres in length and very nearly 1·7 millimetres in diameter. *Slight* unavoidable variations in the jets of different instruments, causing a few seconds difference in the rate of flow, are corrected by slightly varying the height of the pointed stud R which determines the initial head of the oil. A small brass ball-valve fixed to a wire V, when resting in the hemispherical cavity in the agate jet, closes the orifice; when raised so as to allow the oil to flow out, it is suspended, by a small hook, from the stud B. The cylinder A is fixed, by means of a screw thread and leather washer, in the centre of the brazed copper vessel C, which is furnished with a tap D and a copper heating tube E, projecting at an angle of 45° from the side close to the bottom. This vessel contains water or oil, by means of which the temperature of the oil in A is maintained constant, and is provided with a stirring apparatus consisting of four light metal vanes, H, fixed to a thin copper tube which revolves smoothly round the cylinder A, the tube having a broad curved flange at the top to prevent any of the liquid in C from being splashed into the oil in A. The stirrer is rotated to and fro by means of the handle I, and carries with it the thermometer T, which registers the temperature of the fluid bath. Another thermometer T_1, held by a spring clamp which slides on the rod R, is immersed in the oil undergoing test. The instrument is supported on a tripod stand furnished with levelling screws.

Method of Experiment.—The interior of the cylinder A and the orifice of the jet are first inspected. They must be perfectly clean, dry, and free from any loose particles which might obstruct the free flow of the oil. In examining the jet a small mirror held below is useful. After inspection the instrument is levelled. The outer vessel C is then filled with water or heavy mineral oil, according to the temperature at which the viscosity is to be determined, water being used for all temperatures up to about 200° Fahr. The height of the liquid in C should be slightly above that of the oil in A. The temperature of the water-bath having been adjusted, is maintained constant during the test by continual stirring, the thermometer being closely watched, and any tendency of the mercury to rise or fall corrected by additions of colder or warmer water, the excess of water being drawn off through the tap D. Temperatures much above the normal are maintained by heating the tube E, by means of a gas or spirit flame. The oil to be tested, if quite clear and bright, is next poured into A until the point of the stud B is just covered, the jet being first closed by the valve; if the oil is not clear, or if it is a dark-coloured oil, it must first of all be strained through fine wire gauze or muslin. Thick oils may be warmed before straining, but they must not be heated more than a few degrees above the temperature at which the test is to be made. The oil should be brought to nearly the required temperature before being poured into the viscometer, because the adjustment afterwards takes place slowly. The thermometer T_1 is immersed in the oil to such a depth that the bulb does not become uncovered during the test, and it is not afterwards moved. A narrow-necked flask, holding 50 c.c. to a mark on the neck, is placed below the jet to receive the oil. If the test is to be made at a temperature more than a few degrees above or below that of the air of the room, the flask must be immersed in a bath of liquid heated to the testing temperature, or the body of the flask may be surrounded by a thick layer of cotton-wool contained in a beaker, the neck and graduation-mark being left exposed to view. As there is generally a slight leakage from the valve V, the flask should not be placed in position until the last moment.

When *both* thermometers register the desired temperature, the height of the oil in A is finally adjusted so that the point of the stud B lies exactly in the surface, and the measuring flask is placed under the jet. The valve V is then raised, a stop-watch being started at the same moment, and the number of seconds occupied in filling the flask up to the 50 c.c. mark is ascertained. This completes the test. In important cases, and always if the operator be inexperienced, the oil should be poured back into A, a little more being added to bring it up to the mark, and the test repeated, the measuring flask being first rinsed out with ether and dried. Duplicate tests ought not to differ more than about 1 per cent.; greater differences will probably be due to neglect to maintain a constant temperature.

Method of Standardizing.—This instrument is standardized with refined rape oil; but as different samples of genuine rape oil vary in viscosity, Redwood has proposed the adoption of the arbitrary number 535, which is the average number of seconds required by 50 c.c. of rape oil to flow out of his viscometer at 60° F. The relative viscosity at $x°$ F. of any oil, compared with the viscosity at 60° F. of rape oil of density 0·9142,* which is taken as 100, is then found by the following formula:—

$$\text{Relative viscosity (rape oil at 60° F.} = 100) = \frac{td\,100}{535 \times 0{\cdot}9142}$$

where t is the number of seconds required for the outflow of 50 c.c. of the oil at $x°$ F., and d is the density of the oil at the same temperature.

It will be observed that Redwood compares oils at all temperatures with rape oil at 60° F.; some prefer to make the comparison with both oils at the same temperature.

The Coleman-Archbutt Viscometer.†—This instrument, fig. 37, is an improved form of the well-known jacketed glass viscometer first used by Coleman about 1869.‡ It consists of a glass burette contained in an outer jacket, with a funnel for pouring in hot or cold water, a tube for running off water, and a stirrer for thoroughly mixing the water in the jacket. Being made of glass it is fragile; but with reasonable care an instrument may last for many years. It may be standardized with glycerin (see p. 148) so as to give results in absolute measure, and it has the advantage of being very convenient to work with. Thus, the temperature of the oil can be readily adjusted in the efflux-tube itself, by stirring with a thermometer and raising or lowering the temperature of the water in the outer jacket; there is no need for a separate measuring vessel, the volume of oil which flows out being measured by marks on the efflux-tube; a test can be made with as little as 25 c.c. of oil; and after the test has been made the tube is empty and ready for the next test. Oils can be tested in this apparatus at the temperature of boiling water, which is high enough for most purposes.

Construction.—The efflux-tube A is about 15 inches in length. The upper 12 inches is made of thin-walled glass tubing, about 1 inch in internal diameter; it then narrows to a diameter of about $\frac{5}{16}$ inch for 2 inches, and terminates in a thick-walled jet, about 1 inch long and of such internal diameter (about 1·9 mm.) that 100 c.c. of refined rape oil at 60° F. take about ten minutes to run out. If the oil runs too quickly, the orifice of the jet may be slightly closed by fusing the edges in the flame; if too slowly, the jet may be shortened a little. Four circumferential marks are etched upon the tube. The lowest or zero mark is rather above the middle of the narrow portion; the other three marks are on the wide portion and divide the tube above the zero mark into capacities of 25 c.c., 50 c.c., and 100 c.c. The volume of oil used for a test may therefore be varied, according to the viscosity and the quantity of oil available. Of fairly fluid oils, *e.g.*, rape or machinery oils at 60° F., and all oils at 212° F., 100 c.c. are used; of more viscous oils, *e.g.*, cylinder oils at 60° F. and 100° F., 25 c.c. is a suitable quantity. The tube must be separately standardized from each mark, as the times of efflux of the different volumes bear no simple relation to each other.

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* = Sp. gr. 0·915 at $\frac{60°}{60°}$ F.

† Made by Messrs. Baird & Tatlock.

‡ *Jour. Soc. Chem. Ind.*, v. (1886), p. 359.

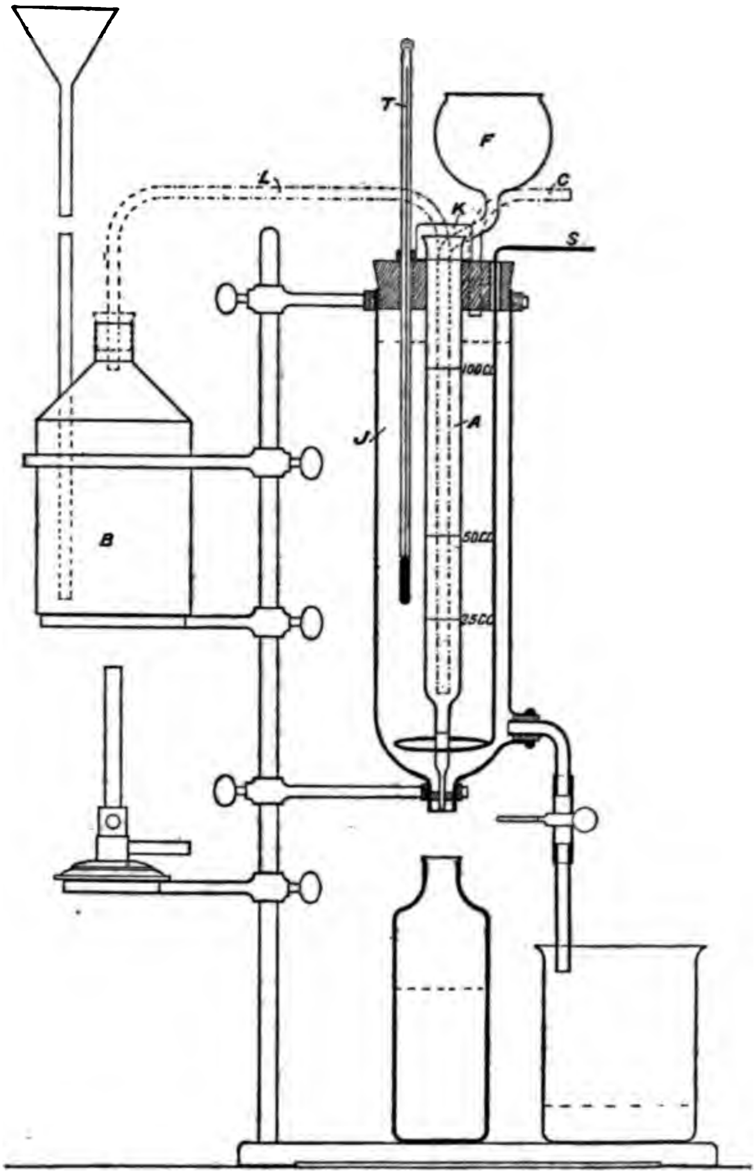

FIG. 37.—THE COLEMAN-ARCHBUTT VISCOMETER.

The outer jacket, J, is about 3½ inches in external diameter, and has a short narrow neck at the bottom and another at the side. The tube, A, is fixed in the jacket by means of a thick indiarubber bung at the top and a thin disc of rubber, not more than $\frac{3}{16}$ inch thick, at the bottom, through which the jet projects not more than $\frac{3}{16}$ inch. Thus, the oil in the tube is surrounded by the water in the jacket until it has reached nearly to the end of the jet, and the temperature is maintained constant until the oil has passed out of the tube. The jet is protected from change of temperature, as well as from fracture, by being contained entirely within the neck of the jacket. The large bung at the top is perforated by four small holes. One, which is lined with a short piece of glass tube, is for the brass stirring wire S; another is for the glass funnel F, which fits rather loosely, and is replaced by a tube L, conveying steam from the boiler B,* for determinations at 212° F.; a third hole is for the bent tube C, for the escape of steam, and the fourth is for the thermometer T.

In putting the apparatus together, the tube A is first wetted and passed through the central hole of the bung, far enough for the jet to reach nearly to the end of the lower neck when the bung is fixed in the jacket; the brass stirring-wire S, which terminates in a brazed ring at the lower end, is then passed through its hole and bent over at the top to form the handle, the bung is then carefully inserted into the jacket and the jet is pushed through the disc of rubber at the lower end. Finally, the tube C is inserted in the bung.

Method of Experiment.—The tube A and jet are first carefully cleaned and dried; the jet is then closed by means of a small peg of soft wood. Water at the proper temperature is next poured into the jacket, and the oil, previously strained, if necessary, and brought to the same temperature, is poured into the efflux-tube up to about half-an-inch above the mark it is intended to run it from. The oil is stirred with a thermometer, avoiding the formation of air-bubbles, until the temperature is exactly correct, the final adjustment being easily made by slightly raising or lowering the temperature of the water-bath. The thermometer is then taken out of the oil, which is allowed to rest until perfectly quiescent. The wood peg is then withdrawn, and the time taken by the oil to flow down to the zero mark is measured by a stop-watch, which is started as the surface of the oil passes the upper mark. During the experiment, the temperature is maintained constant by pouring hot or cold water into the jacket through the funnel and running off the excess through the side tube as often as required, using the stirrer frequently. The temperature of the water in the outer jacket is indicated by the thermometer T, which is not removed. The open end of the efflux-tube is covered by the inverted beaker K, to prevent water from being splashed in by the stirrer.

In making an experiment at 212° F., the cold water in the jacket is first raised gradually to about 180° F., by pouring in hot water, and then the funnel is replaced by the steam tube L, and steam is blown in from the boiler. When the water boils, the level is lowered sufficiently to prevent splashing, and a brisk ebullition is kept up throughout the test. The oil, previously heated to 212° F., should be poured in just before the water begins to boil, and the tube A covered by its cap.

Method of Standardizing.—If the relative viscosity of an oil is required, compared with, say, refined rape oil as the standard, the number of seconds occupied by the oil in flowing out is divided by the number of seconds occupied by the same volume of rape oil in flowing out at the same temperature, a correction being made for the difference in density of the oils. Thus,

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* In the figure this tube is shewn in dotted lines.

$$\text{Relative viscosity} = \frac{td}{t_1 d_1} \times 100,$$

where t and t_1 are the respective times of flow, and d, d_1 are the respective densities of the oils referred to water at 4° C.

For the method of standardizing this viscometer so as to convert the efflux velocities into absolute viscosity values, see p. 148.

Saybolt's Viscometer.—*Construction.*—This instrument is illustrated in fig. 38, and a sectional view shewing the construction of the pipette and the method of fixing it in the outer bath is given in fig. 39. The entire instrument, except the glass tube lining the narrow part of the pipette, and the windows in the outer bath, is of metal. The efflux-tube consists of the wide upper portion A, which is perforated near the top by a ring of small holes a, a, through which the oil can overflow into the fixed gallery B, and the narrow lower portion C, lined with glass tube and terminating in the metal jet J. The metal outer tube of C is cut through so as to form two opposite windows V, through which the oil in the glass tube can be seen. The jet of an instrument, kindly lent to the authors by Mr. Colin Strong of the Anglo-American Oil Company, measured about 9 mm. in length and about 1·6 mm. in internal diameter. The end of the tube C, on which the flange F is soldered, screws into a short tube D, which is soldered into the bottom of the outer bath, and a water-tight joint is made by the washer K.

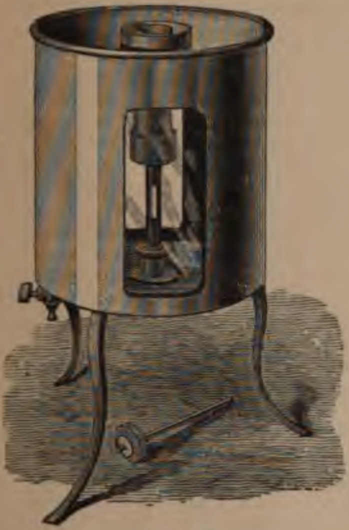

FIG. 38.

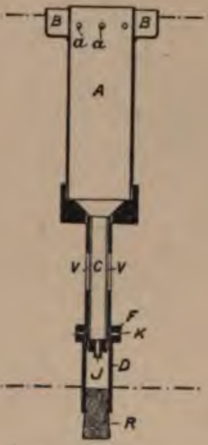

FIG. 39.—SAYBOLT'S VISCOMETER. (Section of Pipette.)

Method of Experiment.—The outer bath is filled with water at the desired temperature, and a cork R is inserted into the end of the tube D. The oil is then poured into A until it overflows into the gallery, and is stirred by a thermometer until the temperature is exactly correct. The thermometer is then removed, allowing the displaced oil to flow back into A, and the excess of oil remaining in the gallery is taken out with a pipette. The cork R is now removed, and the number of seconds which elapses before the surface of the oil is seen through the glass window V is measured by a stop-watch. Redwood gives the following as the relative times of efflux from this instrument and his own at 70° F.

Seconds for 50 c.c. (*Redwood*) = 100
" " x c.c. (*Saybolt*) = 56.

In the instrument lent to the authors, the value of x was 65–67 c.c.

Engler's Standard Viscometer.—*Construction.*—This instrument is shewn in fig. 40. The inner oil vessel A is made of brass, gilt inside, and has a lid A^1, which carries the thermometer t. In the centre of the concave bottom is the jet a, 20 mm. long, 2·9 mm. in diameter at the upper end, tapering to 2·8 mm. at the lower end; it is made of platinum for standard work, but for ordinary work brass is used. The plug valve b, of hard wood, which closes the jet, passes through a tube fixed in the lid and can be raised without removing the cover. Three pointed studs C, fixed at equal distances above the bottom of the vessel, indicate the proper height of the oil, and at the same time serve for levelling the instrument; they mark a volume of 240 c.c. The outer bath B is filled with water when working at temperatures not exceeding 50° C.; above that temperature a heavy mineral oil is used, which can be heated by means of the ring burner d. The oil flowing from the jet is received in the measuring flask C, which has a mark at 200 c.c. and another at 240 c.c.

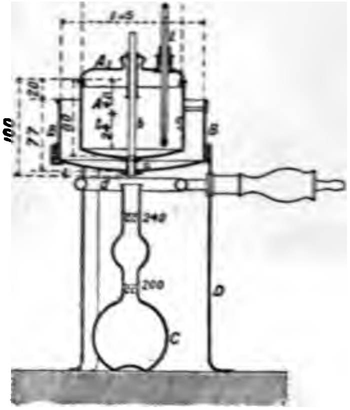

FIG. 40.—ENGLER'S STANDARD VISCOMETER.

Method of Standardizing.—This is done with water at 20° C. The vessel A is first thoroughly rinsed out successively with ether, alcohol, and water, the jet being cleaned by means of a feather or a roll of paper. After the water has drained out, the jet is closed by the valve. The measuring flask is filled to the 240 c.c. mark with water at 20° C., which is then poured into the oil cup A, and should fill it exactly to the level of the studs after the flask has been well drained. The outer bath should be previously filled with water at 20° C. Having adjusted the surface level, if necessary, by taking out or adding a few drops of water, the temperature of the water both inside and outside the cup is brought exactly to 20° C. and then, after allowing time for the water in A to become perfectly still, the plug valve is raised and the water allowed to flow from A into the dry measuring flask. The time of efflux will be from 50 to 53 seconds, if the instrument has been made of the standard dimensions given in the figure. The test must be repeated, and the mean of three experiments which do not differ by more than 0·5 second is the efflux velocity of water at 20° C. The nearest whole number is taken as the unit.

Method of Experiment.—In testing oils, the vessel A and the jet are first thoroughly rinsed with alcohol, then with ether, and dried. The oil, previously strained or filtered to remove suspended matter and water, is poured into A up to the level of the studs, and is stirred by the thermometer until the desired temperature has been reached. The liquid in B is adjusted to the same temperature. After allowing the oil in A to become perfectly still, the plug is raised, and the time required for the outflow of 200 c.c. of oil is noted. Supposing the efflux velocity of water at 20° has been found to be 54 seconds, and the sample of oil required 360 seconds at 50° and 90 seconds at 150°, then the

$$\text{Specific Viscosity } (\textit{Engler}) \text{ at } 50^\circ \text{ C.} = \frac{360}{54} = 6{\cdot}66$$

$$\text{,, \quad ,, \quad ,, \quad } 150^\circ \text{ C.} = \frac{90}{54} = 1{\cdot}66.$$

What Engler calls the 'specific viscosity' is, of course, a purely arbitrary number, obtainable by his instrument alone, and only by such of these as are constructed of the proper dimensions. Instruments recognized by Engler as reliable may be obtained from C. Desaga of Heidelberg, and bear the official mark of the Karlsruhe Chemisch-Technische Versuchsanstalt or the Charlottenburg Technische Anstalt. Engler's viscometer has been adopted by the Committee of the German State Railways.

Holde* finds that in testing thick oils time may be saved by collecting 50 c.c. or 100 c.c., instead of 200 c.c., the results when multiplied by 5 or 2·35 respectively being concordant with those obtained in the ordinary way. He also suggests that the oil-bath should be covered, and a reflux condenser attached so as to condense and return the vapour; liquids of fixed boiling point, such as aniline (184° C.) and naphthalene (217° C.), might then be used for high temperature experiments.

The Engler-Kunkler Viscometer.—*Construction.*—Engler's viscometer has the defect of containing no stirrer, and, when making tests at high temperatures, it is found that the temperature of the oil varies sensibly during efflux. Engler and Kunkler have accordingly designed a modified instrument in which the viscometer and measuring flask are enclosed in a double-walled octagonal air-bath made of stout brass plate, 35 cm. high and 20 cm. wide, figs. 42 and 43. It stands upon four triangular feet, *a*, the outer sloping sides of which rest on the inside edge of the ring of a tripod stand, so that, by shifting the apparatus about, the oil in the cup can be easily levelled. The oven is heated by the flame of a Bunsen burner placed under the copper bottom plate *b*, which has a deep concavity in the centre and is screwed to the bottom flange with an asbestos ring between. Supported above this on the stand *c*, and shielded from direct radiation by the double asbestos disc *f*, is the measuring flask *e*. The viscometer stands upon four legs on the plate *g*, which rests upon a projecting rim; this plate has a hole in the centre for the oil to pass through, and four oval tubes, *i*, reaching above the rim of the oil-vessel, through which and the central hole the heated air from below circulates and maintains a uniform temperature. Glass windows *ll* and *mm* in opposite sides of the casing, and another in the lid, illuminate the interior and enable the necessary observations to be made. Passing through the centre of the cover there is a stirring apparatus, consisting of a tubular axis carrying three blades at the lower end, and furnished with a knob at the upper end by which it is rotated to and fro; stops on the lid prevent it revolving more than one-third of a turn, and also prevent the blades

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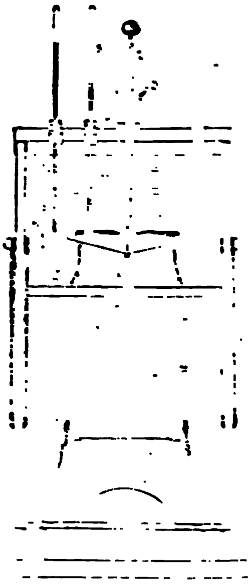
* *Jour. Soc. Chem. Ind.*, xv. (1896), p. 138.

[illegible] therm[illegible] [illegible] the v[illegible] [illegible]ly separat[illegible] [illegible]e, having [illegible] [illegible]e-walled [illegible]

[illegible]ed upon [illegible] [illegible]es and the [illegible] [illegible] viscometer [illegible] The outer therm[illegible]



to 0·5° higher, the oil is quickly poured [illegible] drained, and the tube is then [illegible] face of the oil is level with all the [illegible] whilst the valve rod is held firmly in [illegible] is finally adjusted. The [illegible] its stud, the valve rod is withdrawn [illegible] the number of seconds required to fill the [illegible] exactly noted.

Method of Standardising.—This instrument is standardised [illegible] manner as the Engler viscometer.

The Expression of Viscosity Values

Although viscosity is a definite physical property [illegible] can be accurately ascertained experimentally [illegible] measure, it has been the custom commercially [illegible] duction of mineral lubricating [illegible] other fixed oil as a standard and [illegible] oils with it. From a practical point of [illegible] mended by its simplicity, and [illegible] it is desired to compare it [illegible] case of Redwood's viscometer [illegible] 60° F., the relative efflux [illegible] tional to their relative [illegible] owing to the natural variation in [illegible] same kind of oil even when pure [illegible] which may be caused by the [illegible] standard, a fixed oil is not a [illegible] this objection Redwood has [illegible] principal dimensions of which are fixed [illegible] so as to deliver average rape oil at the same [illegible] want in this country of a central testing [illegible] be properly done, the adjustment of these [illegible] satisfactory. Engler's viscometer [illegible] dimensions, and there water is the standard [illegible] so-called 'specific viscosities,' obtained by dividing the times of [illegible] of oils with that of water, are purely arbitrary numbers, and the same is true of Kunkler's viscosity-numbers [illegible] referred to a standard mixture of glycerol and water of [illegible] viscosity. [illegible] arbitrary numbers may, nevertheless, be sufficient for [illegible] the means of measuring them accurately, and [illegible] common agreement, exists.

Notwithstanding the efforts which have been made to bring about uniformity in the measurement and expression of viscosity values, much difference of practice still prevails. Numbers of viscometers are in use differing from each other in pattern and dimensions, and yielding results which have no meaning to anyone except the possessor of the particular instrument. Results are frequently expressed in seconds, without any information as to the exact significance of the numbers. Thus, although a knowledge of the viscosity of a lubricating oil is one of the most important factors in judging of its suitability for a particular purpose, no generally intelligible method hitherto proposed of expressing the viscosity has met with more than a limited acceptance. The universal adoption of any particular standard instrument giving arbitrary numbers is probably too much to expect. What is wanted is a system of standardizing, which will enable the viscosity of an oil in absolute measure to be deduced from the efflux velocity measured in the ordinary way in any well-designed commercial viscometer. Such a system of standardizing we proceed to explain.

The Standardizing of Commercial Viscometers.

Mixtures of glycerol and water are prepared ranging in viscosity from about 0·05 to about 5·0, a suitable series for the Redwood viscometer being the following:—

TABLE XXXI.

Mixture No.	Glycerol per cent.	Specific Gravity at $\frac{20°}{20°}$ C.	Approximate Viscosity at 20° C.
1	44·4	1·1129	0·046
2	57·0	1·1469	0·086
3	66·0	1·1712	0·157
4	70·6	1·1836	0·228
5	75·3	1·1963	0·350
6	80·4	1·2101	0·596
7	90·8	1·2381	2·39
8	94·8	1·2485	4·73

Mixtures approximating as nearly as possible to these are prepared by weighing and mixing together the required proportions of the purest commercial glycerin and water. The specific gravity of each fluid at $\frac{20°}{20°}$ C. is then carefully determined as directed on p. 166, and each fluid is run from the viscometer in succession at 20° C.,* the experiments being made in duplicate and the mean time taken. Care must be taken to prevent the absorption of water by the stronger glycerins. Finally, pure water is run from the viscometer at 20° C.

Of each fluid we now know—

1. The *viscosity* (η), in dynes per sq. cm. at 20° C., which is ascertained from the table on pp. 134–137;
2. The *time* (t), in seconds, required for the outflow of the standard volume (50 c.c. in the case of Redwood's viscometer) at 20° C.

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* The standardizing *must* be done at *exactly* 20° C., because that is the only temperature at which the values in the table of glycerin viscosities are correct.

3. The *density* (d), which is calculated by multiplying the sp. gr. at $\frac{20^\circ}{20^\circ}$ C. by 0·998259, the density of water at 20° C.

If the viscometer were perfect, the corrected time (td) would be proportional to the viscosity, *i.e.*,

$$ktd = \eta,$$

k being a constant the value of which could be ascertained by running a single fluid of known density and viscosity from the viscometer. But it will be found that the value of k deduced from each of the different fluids (including water) varies, greatly in the case of the thinner fluids, but only slightly with fluids above a certain viscosity, and by plotting the results a curve can be drawn from which the value of k for a fluid of any viscosity can be ascertained. Having constructed such a diagram for any viscometer, a multiplier is obtained by which the '*td*' of any oil, *i.e.*, the time of efflux × the density at the temperature of efflux, may be converted into the viscosity of the oil in dynes per sq. cm. at the temperature of experiment.

We give the results obtained by standardizing in this manner two commercial viscometers, (really four; since the Coleman-Archbutt viscometer may be regarded as three instruments of different capacities having a common jet). See Tables XXXII. and XXXIII.

TABLE XXXII.—THE REDWOOD VISCOMETER.

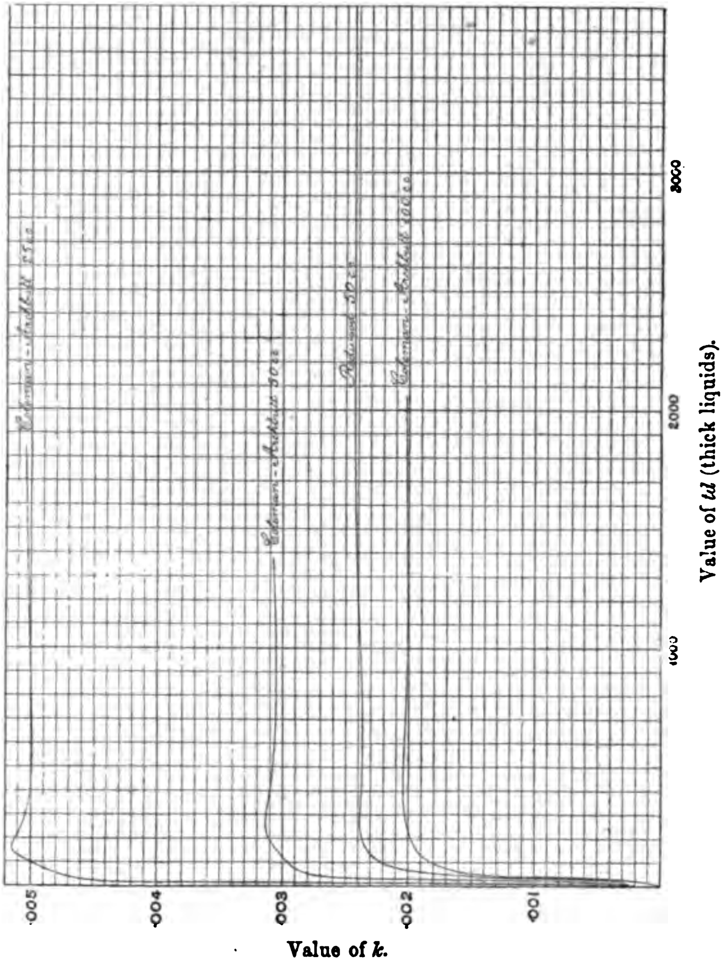
Number and Description of Fluid.		Viscosity at 20° C. η (dynes per sq. cm.).	Time of Efflux at 20° C. t (seconds).	Density of Fluid at 20° C. d.	td.	$\eta \div td = k$.	Variation of k per cent.
1.	Water, .	0·01028	26·0	0·99826	25·95	0·00040	− 83·3
2.	Glycerol and water,	0·0377	33·4	1·0989	36·7	0·00103	− 56·9
3.		0·2360	87·2	1·1828	103·1	0·00229	− 4·2
4.		0·4984	174·7	1·2036	210·3	0·00237	− 0·8
5.		0·7504	259·5	1·2134	314·9	0·00238	− 0·4
6.		1·1123	383·7	1·2218	468·8	0·00237	− 0·8
7.		2·2674	772·7	1·2351	954·4	0·00238	− 0·4
8.		4·0356	1343·0	1·2440	1670·7	0·00242	+ 1·3
9.		8·8370	2900·0	1·2548	3638·9	0·00243	+ 1·7

From the results in these tables it appears that the mean values of k deduced from the efflux velocities of the fluids of 0·4984 viscosity and upwards might be used to calculate the viscosity in absolute measure of all oils exceeding in value 0·49, or we might say of all oils of not less viscosity than sperm oil at 60° F. ($\eta = 0{\cdot}42$), with a maximum error, in the case of either instrument, of ± 2·0 per cent. To enable the viscometers to be used for fluids of lower viscosity,

TABLE XXXIII.—THE COLEMAN-ARCHBUTT VISCOMETER.

Number and Description of Fluid.		Viscosity at 20° C. η (dynes per sq. cm.).	Time of Efflux at 20° C. t (seconds).	Density of Fluid at 20° C. d.	td.	$\eta \div td = k$.	Variation of k per cent.
			100 c.c.				
1.	Water.	0·01028	28·10	0·998259	28·05	·00037	− 81·7
2.	Glycerol and water.	·0377	36·25	1·0989	39·8	·00095	− 53·0
3.		·2338	104·6	1·1825	123·7	·00189	− 6·4
4.		·4984	205·9	1·2036	247·8	·00201	− 0·5
5.		·7504	303·1	1·2134	367·8	·00204	+ 1·0
6.		1·1123	446·2	1·2218	55·2	·00204	+ 1·0
7.		2·2674	913·8	1·2351	1128·6	·00201	− 0·5
8.		4·0356	1604·5	1·2440	1996·0	·00202	± 0·0
			50 c.c.				
2.	Glycerol and water.	·0377	22·05	1·0989	24·2	·00156	− 49·4
3.		·2338	67·65	1·1825	80·0	·00292	− 5·2
4.		·4984	135·15	1·2036	162·7	·00306	− 0·6
5.		·7504	197·7	1·2134	239·9	·00313	+ 1·6
6.		1·1123	292·85	1·2218	357·8	·00311	+ 1·0
7.		2·2674	601·2	1·2351	742·5	·00305	− 1·0
8.		4·0356	1056·5	1·2440	1314·3	·00307	− 0·3
			25 c.c.				
2.	Glycerol and water.	·0377	12·7	1·0989	14·0	·00269	− 46·6
3.		·2338	41·45	1·1825	49·0	·00477	− 5·4
4.		·4984	82·95	1·2036	99·8	·00499	− 1·0
5.		·7504	120·4	1·2134	146·1	·00514	+ 2·0
6.		1·1123	178·4	1·2218	218·0	·00510	+ 1·2
7.		2·2674	369·1	1·2351	455·9	·00497	− 1·4
8.		4·0356	648·5	1·2440	806·7	·00500	− 0·8
9.		8·8370	1396·0	1·2548	1751·7	·00504	± 0·0

uch, *e.g.*, as rape oil at 150° F. ($\eta = 0·18$) or cylinder oils at 212° F. $\eta = 0·16$ to $0·31$), the results have been plotted on diagrams. Fig. 44 ives the complete curves for all liquids. Fig. 45 gives, on an enlarged ale, the first part of each curve for thin liquids.*



The success of this method of standardizing depends upon the flow f liquid through the jet of the viscometer being free from eddying motion, and provided the length of the jet does not exceed twenty times its diameter steady motion may be relied upon in the case of liquids of not lower viscosity than 0·4. With thinner liquids unsteady

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* These diagrams are, of course, applicable only to the particular instruments or which they were constructed.

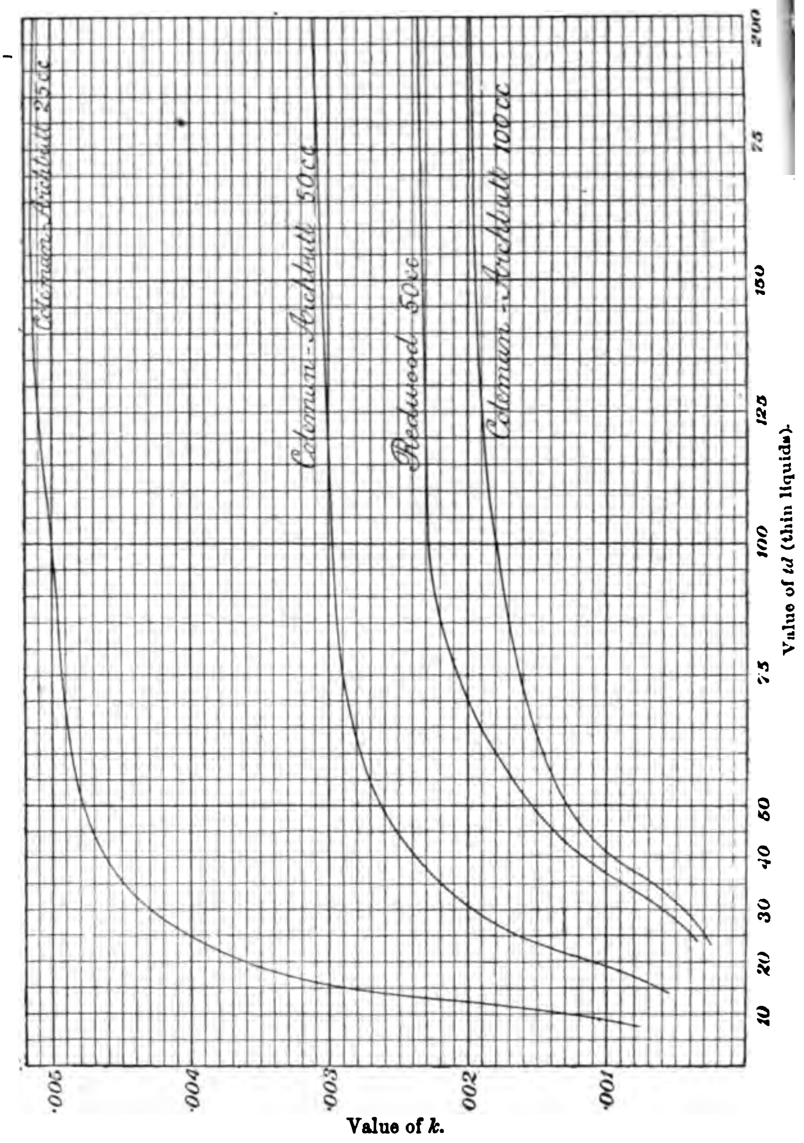


FIG. 45.—CORRECTION CURVE FOR THE COLEMAN-ARCHBUTT AND REDWOOD VISCOMETERS.

motion may occur, and the tendency to form eddies will be greater, *cæteris paribus*, the higher the density of the liquid and the lower its viscosity. That is to say, the comparatively heavy glycerol solutions used for standardizing will be more likely to set up eddies than the lighter oils, and consequently the latter may flow more rapidly than glycerol solutions of equal viscosity. With both the viscometers tested by us this has been found to be the case, and the value of *k* corresponding to the *td* of thin oils is too small to give the true viscosity. If, however, the value of *k* corresponding to $1\frac{2}{5}$ *td* be taken, practically correct results are obtained, even with oils as thin as water. We therefore apply this correction to all thin oils. The following rules contain a summary of the method :—

RULES FOR DETERMINING BY MEANS OF A STANDARDIZED VISCOMETER THE VISCOSITY OF A LUBRICATING OIL IN ABSOLUTE MEASURE AT ANY DESIRED TEMPERATURE.

A. For Oils of Viscosity 0·4 and upwards.

1*st. Determine the time of efflux* (*t*) *of the standard volume in seconds.*

2*nd. Determine the density* (*d*) *of the oil at the same temperature.*

3*rd. Find the value of k corresponding to td.*

4*th. Multiply td by k ; the product is the absolute viscosity.*

B. For Oils of Lower Viscosity than 0·4.

1*st and* 2*nd. As above.*

3*rd. Find the value of k corresponding to* $\frac{7td}{5}$.

4*th. Multiply td by k; the product is the absolute viscosity.*

The following results shew the accuracy of which the method is capable. Oils of low viscosity were selected for experiment, as with these the error is likely to be greatest.

Description of Oil.	Density at 20° C.	Absolute Viscosity at 20° C., determined by means of the		
		Absolute Viscometer.	Redwood Viscometer.	Coleman Viscometer.
Mixture of shale oil and petroleum, . . .	0·8265	0·040	0·040	0·042
Shale oil, ...	0·8653	0·124	0·123	0·122
Sperm oil, ...	0·8783	0·377	0·377	0·378

Tables XXXIV. and XXXV. contain the complete results obtained by testing in this manner a number of lubricating oils. A summary is given in Table XXXVI. The curves in figs. 46, 47, 48, 49 show the relation between absolute viscosity and temperature in the case of mineral lubricating oils, as compared with typical animal and vegetable oils.

TABLE XXXIV.—VISCOSITIES OF OILS IN DYNES PER SQ. CM. DETERMINED BY THE COLEMAN-ARCHBUTT VISCOMETER.

Description of Oil.	60° F.				
	Efflux Velocity (Seconds) t.	Density d.	td.	k.	Viscosity η $=ktd$.
Animal and Vegetable Oils.	100 c.c.				
Sperm oil, ...	240·4	·8783	211·1	·00199	0·420
Olive oil, ...	539·2	·9159	493·9	·00204	1·008
Rape oil, ...	598·6	·9151	547·8	·00204	1·118
Tallow, ...	...	...	...	...	...
Castor oil, ...	...	...	...	...	...
Scotch Mineral Oils.					
'865,'	90·7	·8683	78·8	·00185	0·146
'890,'	284·4	·8905	253·3	·00201	0·509
Russian Mineral Oils.					
Refined light machine oil, .	631·3	·8978	566·8	·00204	1·156
,, heavy machine oil, .	1955·0	·9096	1778·3	·00202	3·592
American Mineral Oils.					
Pale, '885/90,'	256·2	·8844	226·6	·00200	0·453
Spindle oil (stainless), '860/70,'	410·5	·8677	356·2	·00204	0·727
Pale, '903/7,'	619·5	·9008	558·1	·00204	1·138
Red engine oil, '910/20,' .	1040·0	·9162	952·8	·00201	1·915
'Bayonne' engine oil, '912/15,'	1185·6	·9113	1080·5	·00201	2·172
	50 c.c.				
Dark medium machinery oil, .	1130·0	·8839	998·8	·00305	3·046
'Valvoline' cylinder oil, .	...	...	...	...	...
Filtered cylinder oil, '885/90,' .	...	...	...	...	...
,, ,, '888,' .	...	...	...	...	...
Dark cylinder oil, '890/5,' .	...	...	...	...	...

Table XXXIV.—Viscosities of Oils in Dynes per sq. cm. determined by the Coleman-Archbutt Viscometer—*continued.*

Description of Oil.	100° F.				
	Efflux Velocity (Seconds) *t.*	Density *d.*	*td.*	*k.*	Viscosity η =*ktd.*
Animal and Vegetable Oils.	100 c.c.				
Sperm oil,	111·7	·8637	96·5	·00192	0·185
Olive oil,	208·2	·9011	187·6	·00201	0·377
Rape oil,	235·6	·9005	212·2	·00199	·422
Tallow,	...	...	...	...	...
Castor oil,	1433·0	·9473	1357·5	·00201	2·729
Scotch Mineral Oils.					
'865,'	52·0	·8533	44·4	·00148	0·066
'890,'	108·9	·8761	95·4	·00192	0·183
Russian Mineral Oils.					
Refined light machine oil,	174·9	·8837	154·6	·00199	0·307
" heavy machine oil,	417·0	·8957	373·5	·00204	0·762
American Mineral Oils.					
Pale, '885/90,'	99·2	·8700	86·3	·00188	0·162
Spindle oil (stainless), '860/70,'	141·0	·8535	120·3	·00196	0·236
Pale, '903/7,'	193·0	·8867	171·1	·00200	0·342
Red engine oil, '910/20,'	273·4	·9020	246·6	·00201	0·496
'Bayonne' engine oil, '912/15,'	315·4	·8973	283·0	·00202	0·572
Dark medium machinery oil,	397·6	·8695	345·7	·00204	0·705
	50 c.c.				
'Valvoline' cylinder oil,	901·0	·8757	788·9	·00305	2·406
	25 c.c.				
Filtered cylinder oil, '885/90,'	684·7	·8708	596·2	·00499	2·975
" " '888,'	848·8	·8724	740·5	·00500	3·702
Dark cylinder oil, '890/5,'	955·0	·8846	844·8	·00500	4·224

TABLE XXXIV.—VISCOSITIES OF OILS IN DYNES PER SQ. CM. DETERMINED BY THE COLEMAN-ARCHBUTT VISCOMETER—*continued.*

Description of Oil.	150° F.				
	Efflux Velocity (Seconds) t.	Density d.	td.	k.	Viscosity $\eta = ktd$.
Animal and Vegetable Oils.	100 c.c.				
Sperm oil, ...	62·1	·8455	52·5	·00161	0·085
Olive oil, ...	93·3	·8826	82·3	·00187	0·154
Rape oil, ...	105·2	·8822	92·8	·00191	0·177
Tallow, ...	105·2	·8784	92·4	·00190	0·176
Castor oil, ...	321·2	·9284	298·2	·00203	0·605
Scotch Mineral Oils.					
'865,'	38·2	·8347	31·9	·00113	0·036
'890,'	54·8	·8581	47·0	·00146	0·069
Russian Mineral Oils.					
Refined light machine oil, .	67·9	·8661	58·8	·00168	0·099
„ heavy machine oil, .	115·4	·8784	101·4	·00193	0·196
American Mineral Oils.					
Pale, '885/90,'	52·2	·8521	44·5	·00148	0·066
Spindle oil (stainless), '860/70,'	63·9	·8358	53·4	·00162	0·086
Pale, '903/7,'	75·5	·8690	65·6	·00175	0·115
Red engine oil, '910/20,' .	91·9	·8843	81·3	·00185	0·150
'Bayonne' engine oil, '912/15,'	103·5	·8797	91·1	·00190	0·173
Dark medium machinery oil, .	127·0	·8514	108·1	·00194	0·210
'Valvoline' cylinder oil, .	347·0	·8587	298·0	·00203	0·605
Filtered cylinder oil, '885/90,' .	...	...	...	...	...
„ „ '888,' .	...	...	...	...	...
Dark cylinder oil, '890/5,' .	471·4	·8666	408·5	·00204	0·833

TABLE XXXIV.—VISCOSITIES OF OILS IN DYNES PER SQ. CM. DETERMINED BY THE COLEMAN-ARCHBUTT VISCOMETER—*concluded.*

Description of Oil.	212° F.				
	Efflux Velocity (Seconds) *t.*	Density *d.*	*td.*	*k.*	Viscosity η $= ktd.$
Animal and Vegetable Oils.					
	100 c.c.				
Sperm oil,	43·4	·8229	35·7	·00128	0·046
Olive oil,	53·6	·8596	46·1	·00151	0·070
Rape oil,	58·7	·8595	50·5	·00158	0·080
Tallow,	58·0	·8557	49·6	·00157	0·078
Castor oil,	98·9	·9050	89·5	·00189	0·169
Scotch Mineral Oils.					
'865,'	...	...	...	...	...
'890,'	...	...	...	...	...
Russian Mineral Oils.					
Refined light machine oil,	41·0	·8442	34·6	·00124	0·043
„ heavy machine oil,	51·8	·8568	44·4	·00148	0·066
American Mineral Oils.					
Pale, '885/90,'	36·8	·8298	30·5	·00107	0·033
Spindle oil (stainless), '860/70,'	40·8	·8138	33·2	·00119	0·039
Pale, '903/7,'	43·8	·8469	37·1	·00132	0·049
Red engine oil, '910/20,'	47·5	·8624	41·0	·00142	0·058
'Bayonne' engine oil, '912/15,'	50·4	·8579	43·2	·00146	0·063
Dark medium machinery oil,	59·1	·8291	49·0	·00156	0·076
'Valvoline' cylinder oil,	116·0	·8377	97·2	·00192	0·187
Filtered cylinder oil, '885/90,'	100·1	·8306	83·1	·00186	0·155
„ „ '888,'	145·2	·8351	121·3	·00196	0·238
Dark cylinder oil, '890/5,'	145·0	·8441	122·4	·00196	0·240

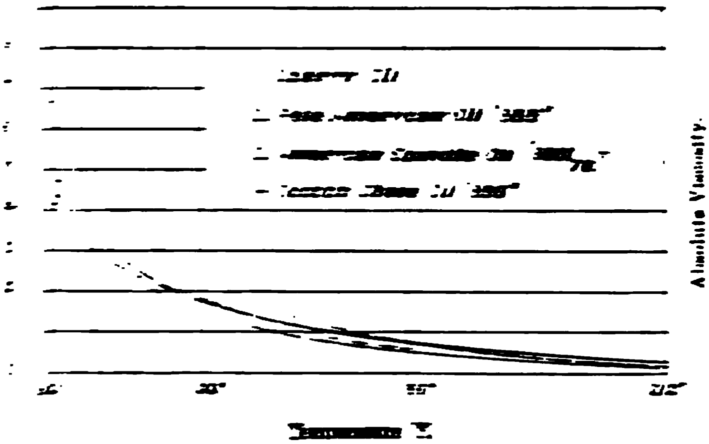
TABLE XXXV.—VISCOSITIES OF OILS IN DYNES PER SQ. CM. DETERMINED BY THE REDWOOD VISCOMETER.

Description of Oil.	Efflux Velocity (Seconds) t.	Density d.	td.	k.	Viscosity η = ktd.
			60° F.		
American Mineral Oils.					
'Globe' oil	653·0	·8802	574·8	·00237	1·362
Pale 907 12	689·5	·9054	624·3	·00237	1·479
Dark N cylinder oil, 895 900	...	...	...	...	...
Dark filtered N cylinder oil, 900	...	...	...	...	...
Dark locomotive cylinder oil, 896	...	...	...	...	...
			100° F.		
American Mineral Oils.					
'Globe' oil	199·6	·8663	173·0	·00234	0·405
Pale, 907 12.	200·2	·8915	178·5	·00235	0·419
Dark N cylinder oil, 895 900,	2629·5	·8810	2316·7	·00243	5·630
Dark filtered N cylinder oil, 900	2902·0	·8883	2577·9	·00243	6·264
Dark locomotive cylinder oil, 896	3000·0	·8836	2650·7	·00243	6·441
			212° F.		
American Mineral Oils.					
'Globe' oil, ...	...	...	...	...	...
Pale, 907 12, ...	...	...	...	...	...
Dark N cylinder oil, 895 900,	139·8	·8417	117·7	·00234	0·275
Dark filtered N cylinder oil, 900	157·3	·8490	133·6	·00235	0·314
Dark locomotive cylinder oil, 896	155·5	·8441	131·3	·00235	0·308

TABLE XXXVI.—ABSOLUTE VISCOSITIES OF OILS (SUMMARY).

Description of Oil, etc.	Absolute Viscosity (η) in Dynes per sq. cm.			
	60° F.	100° F.	150° F.	212° F.
Water at 68° F. (20° C.), . .	0·01028			
Animal and Vegetable Oils.				
Sperm oil, ...	0·420	0·185	0·085	0·046
Olive oil, ...	1·008	0·377	0·154	0·070
Rape oil, ...	1·118	0·422	0·177	0·080
Tallow, ...	...	...	0·176	0·078
Castor oil, ...	...	2·729	0·605	0·169
Scotch Mineral Oils.				
'865,'	0·146	0·066	0·036	...
'890,'	0·509	0·183	0·069	...
Russian Mineral Oils.				
Refined light machine oil, 895/900,	1·156	0·307	0·099	0·043
„ heavy „ 905/10,	3·592	0·762	0·196	0·066
American Mineral Oils.				
Pale, '885/90,'	0·453	0·162	0·066	0·033
Spindle oil (stainless), '860/70,' .	0·727	0·236	0·086	0·039
Pale, '903/7,'	1·138	0·342	0·115	0·049
'Globe' oil (dark), . . .	1·362	0·405	...	...
Pale, '907/12,'	1·479	0·419	...	...
Red engine oil, '910/20,' . .	1·915	0·496	0·150	0·058
Bayonne engine oil, '912/15,' .	2·172	0·572	0·173	0·063
Dark medium machinery oil, .	3·046	0·705	0·210	0·076
'Valvoline' cylinder oil, . .	...	2·406	0·605	0·187
Filtered cylinder oil, '885/90,' .	...	2·975	...	0·155
„ „ '888,' . .	...	3·702	...	0·238
Dark A cylinder oil, '890/5,' .	...	4·224	0·833	0·240
„ N „ '895/900,' .	...	5·630	...	0·275
„ filtered N cylinder oil, '900,'	...	6·264	...	0·314
„ locomotive „ '896,'	...	6·441	...	0·308

[illegible]


Absolute Viscosity.
212°

[illegible]

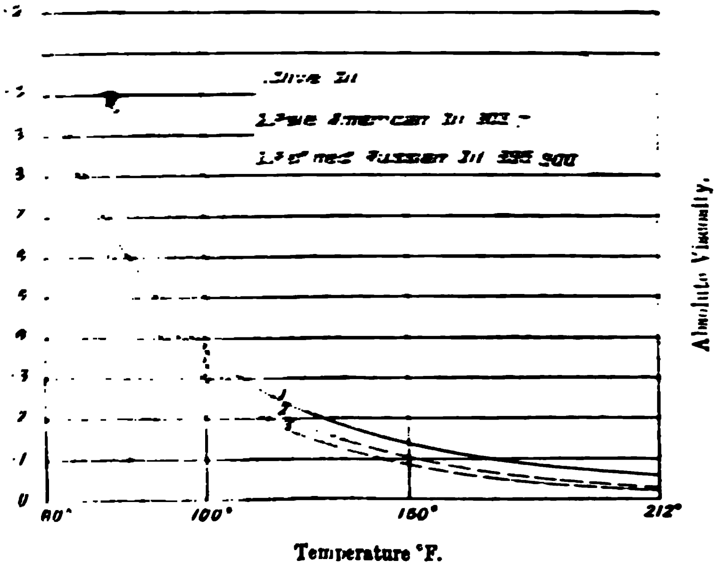

Olive Oil
American Oil
Oil
.1
.2
.3
0
80°
100°
150°
212°
Temperature °F.
Absolute Viscosity.

FIG. 48.—HEAVY MACHINERY OILS.

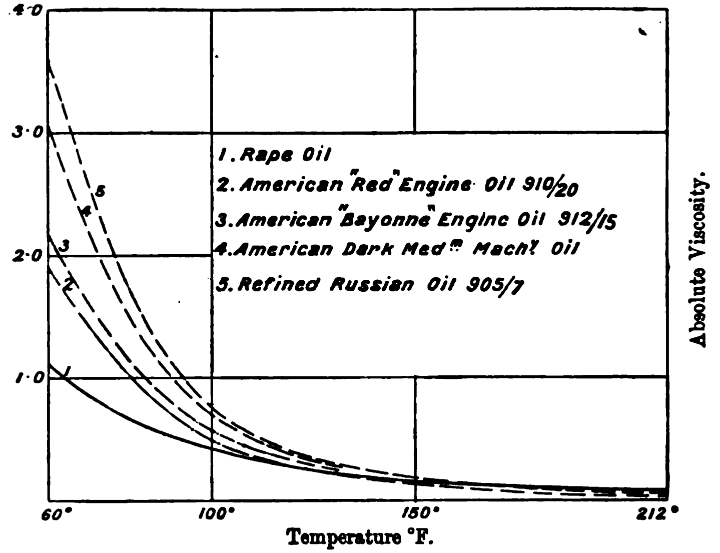
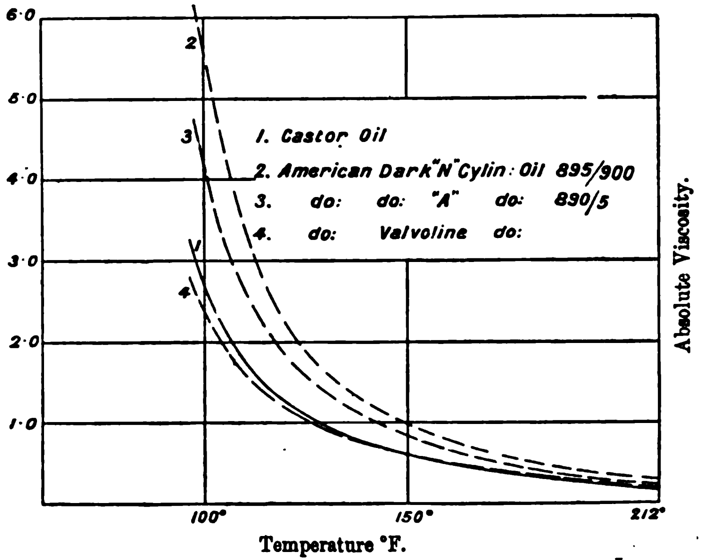


FIG. 49.—CYLINDER OILS.



[illegible]

[illegible] is arrested. [illegible] is commenced, [illegible] commences to [illegible] brackets [illegible] rests upon [illegible] is noted. The [illegible] The piston is loaded [illegible] 200 grammes, one [illegible] grammes, according to the consistence of the [illegible] by the rod and disc *p*. The weight [illegible] grammes.

In using this apparatus, the tube *c* is filled with the grease to be tested by first inserting the piston *e* and spreading the grease with a broad knife upon the disc *b*, and, whilst spreading more and more grease, gradually withdrawing the piston until the upper disc reaches the open end of the tube.

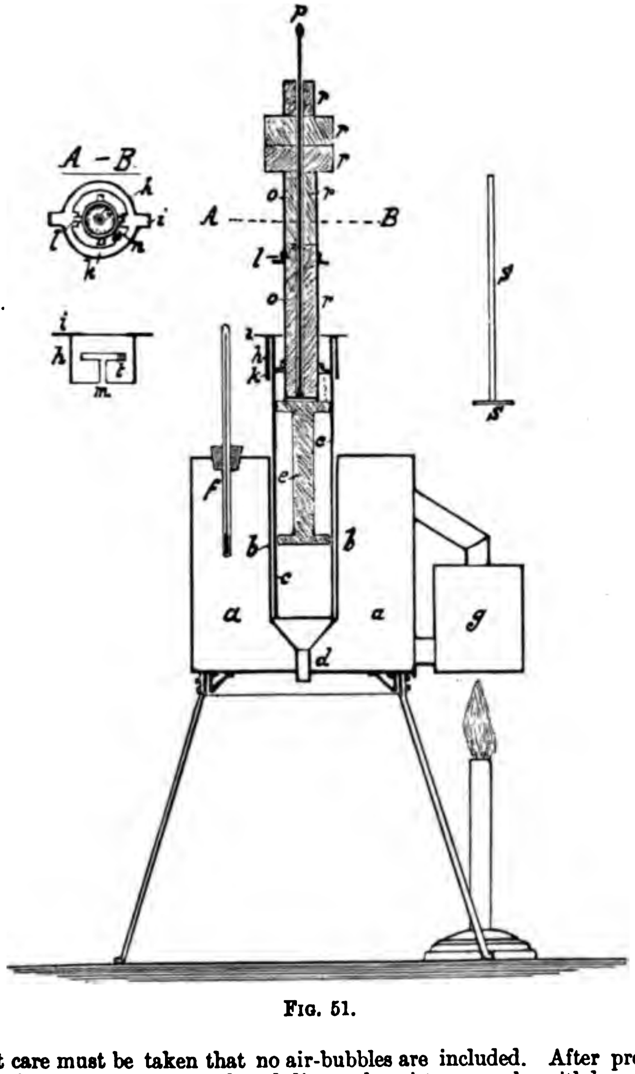


FIG. 51.

Great care must be taken that no air-bubbles are included. After pressing down the grease with the rod and disc *s*, the piston may be withdrawn and another tube filled, as, owing to the extent to which the consistency of grease is affected by working it about, the tube after filling must remain for at least 24 hours at a temperature of about 20° C. before the test is made. The water-bath is then filled nearly full of water at 55° C., and this temperature is maintained constant during the test. The tube of grease having been inserted into the fixed tube *b*, the piston is put in and pressed down until the stop *k* rests upon the cap. After the lapse of 20 minutes the suitably loaded piston is liberated by turning the cap, and the time which elapses before its movement is arrested by the stops *l* measures the consistency of the grease.

This apparatus is intended for comparing the consistency of one sample of grease with another, or of several samples with a standard, and the load put upon the piston must depend upon the consistency of the grease. It should be so proportioned that the time of experiment with the stiffest sample is about 10 minutes. It is obvious that the load must be the same for all samples compared, as the results of tests made with different loads do not admit of comparison.

B.—SPECIFIC GRAVITY AND DENSITY.

The specific gravity of a solid or liquid substance is the weight compared with that of an equal volume of water taken as unity. Unless otherwise stated, the comparison is made with water at the same temperature as the substance, but such an expression as 'sp. gr. at $\frac{20^\circ}{4^\circ}$' means the weight of the substance at 20° compared with water at 4° taken as unity. In the C.G.S. system of units, the specific gravity at $\frac{20^\circ}{4^\circ}$ C. is identical with the *density* of the substance at 20° C.*

The specific gravities of the vegetable and animal oils and fluid waxes at 60° F. (15·5° C.) range from about 0·879, in the case of sperm oil, to about 0·968 in that of castor oil, and, although individual specimens of each description of oil are liable to vary somewhat in specific gravity, the limits of variation for each of the principal kinds of oil are not wide and are pretty well known. Hence, a knowledge of the specific gravity of an animal or vegetable oil is valuable both as a means of identification and also in judging of the purity of a particular specimen.

Mineral lubricating oils may also be classified according to their specific gravities (see p. 177), though this property is not of material importance in relation to their lubricating value. It is, however, of great importance in distinguishing between mineral oils, on the one hand, and rosin and coal-tar oils on the other.

Determination of Specific Gravity.—Practically three methods are in use for determining the specific gravity of liquids, viz.:—1. *By pyknometers.* 2. *By the specific gravity balance.* 3. *By hydrometers.* The first method is applicable to all liquids, however viscous, and is therefore the most suitable for lubricating oils. The two last methods are adapted only for liquids of very moderate viscosity, and their applicability to lubricating oils is therefore limited.

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* See Tait, *Properties of Matter*, 3rd edit., p. 30.

The term 'pyknometer' includes any vessel in which an accurately measured volume of a liquid can be weighed; the kinds in common use are the various forms of specific gravity bottle and the Sprengel tube. Of the former, the plain form, with an accurately ground, finely perforated stopper, is most useful for determining the specific gravities of lubricating oils at ordinary temperatures; for higher temperatures, and for limited quantities of material, the Sprengel tube is more convenient and accurate.

Bottle Method.—The specific gravity bottle with perforated stopper is shewn in fig. 52. It can be obtained of various sizes, but the most suitable for our purpose holds nominally 25 grammes of water at 60° F. The capacity marked on the bottle must not be accepted without verification, but the bottle must be calibrated by ascertaining its weight, when empty, and when filled with recently boiled distilled water at 60° F.

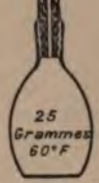

FIG. 52.

To calibrate the bottle.—The bottle before being weighed must first be thoroughly cleaned, rinsed with water, alcohol and ether in succession, then warmed, and dried by aspirating a current of air to displace the ether vapour. The bottle should not be strongly heated. The stopper, also cleaned and dried, is inserted; the bottle is allowed to stand in a cool place for 10 or 15 minutes, then wiped with a clean soft rag and immediately weighed. Some pure distilled water is next boiled vigorously for about 5 minutes in a platinum or silver vessel, rapidly cooled to 60° F., and carefully poured into the bottle, avoiding the introduction of air bubbles. The bottle is immediately immersed up to the neck in a capacious basin of water at exactly 60° F., and is allowed to stand at this temperature for a few minutes, the water in the basin being frequently stirred with the thermometer and maintained constant in temperature. The stopper is then inserted in the bottle, well bedded into its seat, and the surplus water which has exuded through the perforation wiped off. If now the temperature of the water is the same inside and outside the bottle, the capillary in the stopper will remain exactly full, and there will be neither contraction nor exudation of water. When this is the case, the bottle is lifted out of the water in the basin, and slowly immersed * in water several degrees colder, which will cause the water in the bottle to contract and empty the capillary; the outside of the bottle can now be wiped quite dry and weighed before the water has time to expand and exude from the stopper. Duplicate weighings, if carefully made in the manner directed, will not differ by more than two or three tenths of a milligramme. At least two weighings should be made. The bottle is then dried and again weighed empty. The weight should not differ from the previous weight of the empty bottle by more than 0·5 milligramme. The difference between the mean weight of the bottle when full and empty is the *water capacity of the bottle at 60° F.* This seldom needs to be redetermined; but the empty bottle should be frequently reweighed, as it may become scratched or chipped in use.

To determine the specific gravity of oil at 60° F.—About 50 c.c. of the oil are poured into a small lipped beaker, stirred with a thermometer, most carefully avoiding the introduction of air bubbles, and brought to exactly 60° F. by immersing the beaker in water 2 or 3 degrees above or below that temperature. The bottle is then filled quite full of the oil, without introducing any air bubbles, immersed up to the neck in water at 60° F., the stopper loosely inserted, causing the excess of oil to overflow into the basin, and then, after waiting about five minutes, bedded firmly into its place, the excess of oil being wiped off the top of the stopper. Having ascertained that the temperature is correct, and that the oil is neither expanding nor contracting, the bottle is cooled, wiped clean and dry, and weighed, exactly as in calibrating the bottle with water. By subtracting from the total weight the tare of the empty bottle, and then dividing the difference by the water capacity of the bottle, the specific gravity of the oil at 60° F. is obtained. The thermometer used must be verified by comparison with a standard instrument.

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* Rapid immersion, by causing the bottle to contract first, expels some liquid from the stopper.

Glycerin and very viscous liquids which cannot be poured into the narrow neck of the bottle may be manipulated as follows:—The jet is cut off a 30 c.c. pipette, making the delivery nozzle the full bore of the tube, and the dry pipette is filled with the liquid. The nozzle of the pipette having been wiped outside, is then inserted into the specific gravity bottle nearly to the bottom, and the liquid is allowed to quietly flow out. In this way the bottle may be easily filled without the introduction of a single air bubble. The bottle, whilst being filled, is held down in water at the required temperature, and, when full, the stopper is inserted, and the bottle is allowed to stand in the water at constant temperature until expansion or contraction has ceased. The excess of fluid is then removed from the stopper, the bottle is cooled, wiped clean and dry, and weighed.

Sprengel Tube Method.— Sprengel's very useful pyknometer has the form of an elongated U, the arms of which terminate in two capillary tubes which are bent at right angles in opposite directions. One of the capillary tubes has a very fine bore and is drawn down to a point, the other has a wider bore, about 0·5 mm. in diameter, and is not drawn down.

In filling the tube, a small glass bulb, with a piece of narrow rubber tubing attached to it, is fixed on to the narrower capillary by means of a perforated rubber stopper, and the wider capillary is dipped into the oil, which is then drawn into the tube by suction applied to the rubber tube, the glass bulb serving as a vacuum chamber. This is the method described by Sprengel,* but with liquids of moderate viscosity the glass bulb may be dispensed with, and viscous liquids can usually be reduced in viscosity by warming, so as to be easily drawn into the tube. When full, the tube is detached from the bulb and suspended in a beaker of water, as shewn in fig. 53, and the temperature of the water is maintained constant with frequent stirring until the liquid has ceased to expand or contract. It is most convenient to arrange the temperature of the liquid in the tube so that it shall expand, and the liquid is absorbed by a strip of filter paper until it ceases to exude from the capillary orifice. The tube is then lifted out of the water by means of a small brass wire hook, and immersed for a short time in colder water, so as to contract the liquid and empty the capillaries. It is then wiped and weighed.

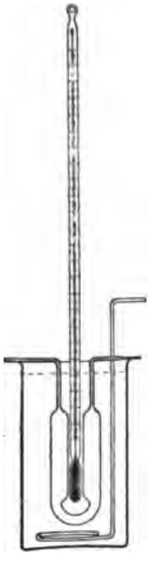

FIG. 53.

The movement of the liquid in expanding or contracting takes place as a rule entirely through the wider capillary, where there is least resistance. The narrower capillary, when full, generally remains so, and no liquid is expelled from it unless expansion occurs very rapidly. If it is necessary to introduce liquid into the pyknometer, owing to contraction having occurred, a drop in the end of a glass tube applied to the point of the narrow capillary will be drawn in.

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* *Jour. Chem. Soc.*, 1873, p. 577.

The water capacity of this pyknometer is determined as in the case of the bottle, and having been done with great care need seldom be redetermined, but the empty tube should be reweighed occasionally.

At 212° *F.* (=100° *C.*).—For determining the sp. gr. of oils at the boiling point of water, which for all practical purposes may be assumed to be 212° F., the neck of a 40-oz. flask is cut down as shewn in fig. 54, and two opposite nicks are filed in the rim to receive the arms of the Sprengel tube. The flask is filled to the depth of about two inches with hot water, a few fragments of pumice are thrown in, and the water is made to boil vigorously. The filled Sprengel tube is then suspended in the steam, and the open neck of the flask is covered by a watch glass. As soon as oil is no longer expelled from the tube, the ends of the capillary arms are wiped with filter paper and the tube is lifted out of the steam, cooled by immersion in cold water, wiped and weighed. This is the most convenient method of determining the specific gravities of fatty acids and fats which are solid at the ordinary temperature.

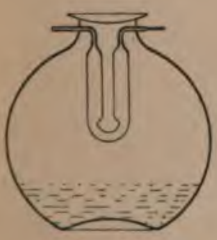

FIG. 54.

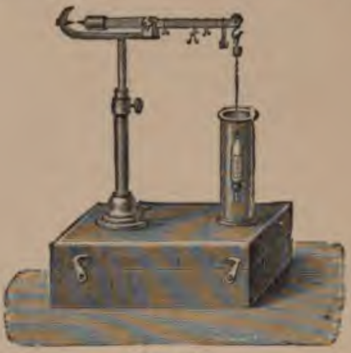

FIG. 55.

Sprengel tubes may be made to hold as little as 1 c.c., and with care the results obtained with a delicate balance are surprisingly accurate. Such small tubes are sometimes useful for determining the specific gravity of the limited quantities of fatty acids obtained by saponifying mixed oils in the process of analysis. Sprengel pyknometers are specially adapted for work with hot liquids, as they need not, like bottles, be handled, and their shape causes the temperature of the contained liquid to become quickly adjusted. The movement of the liquid in the delicate capillary tubes indicates the slightest variation of temperature. The only drawback is the tedious nature of the filling and emptying operations with viscous liquids, but this may be largely overcome by warming the liquid so as to reduce the viscosity.

Westphal Balance Method.—The Westphal specific gravity balance (fig. 55) is an instrument of the steelyard type constructed to indicate the specific gravity of a liquid by the relative loss of weight of a plummet of known displacement when suspended in the liquid. The complete instrument consists of the balance proper, the glass thermometer-plummet, the immersion cylinder, and two exactly similar sets of four rider weights, the largest rider of each set having the same weight as the water which the plummet displaces at 60° F., the next rider having one-tenth of this weight, the third one-hundredth, and the fourth one-thousandth. The beam is divided by notches into ten exactly equal parts, the notches being points of suspension for the riders and numbered consecutively from 1 to 9.

The balance is set up in a place free from draughts, and is adjusted by means of the levelling screw in the foot, so that when the beam is oscillating with the plummet suspended in air the index finger at the short end of the beam will come to rest exactly opposite to the fixed point. If the plummet be now suspended in water at 60° F., assuming that the instrument is intended for use at that temperature, equilibrium will be exactly restored by suspending one of the largest riders from the same hook as the plummet, indicating a specific gravity of 1·0. But if the liquid be of specific gravity 0·90, equilibrium will be restored by suspending the same rider from notch No. 9; if the specific gravity be 0·92, the next largest rider also must be suspended from notch No. 2; if the specific gravity be 0·922, the third rider must be hung from the second; and if the specific gravity be 0·9225, the smallest rider must be hung from notch No. 5. Thus the specific gravity of any liquid is shewn at a glance to four decimal places by the positions of the riders on the beam, the largest rider giving the first decimal place and the other riders the remaining places in order.

Every instrument purchased must, before use, be verified by measuring carefully the distances between the fixed points along the beam, which should not vary more than one-thousandth part. The plummet must also be weighed in air and in water at 60° F. on a good ordinary balance indicating 0·1 milligramme, and the water displaced by the plummet must weigh the same as the largest rider of each set, the other riders varying in decimal proportion. The following table by Stock shews the variations met with in the riders of a Westphal balance by a good maker, the numbers in the third column shewing that the maximum deviation from unity did not exceed 1 unit in the fourth decimal place, which is a satisfactory agreement.

TABLE XXXVII.—SHEWING VARIATIONS IN RIDERS.

Rider Number.	Weight in Air. Grammes.	Relation to Unity. Plummet Displacement = 6·48 Grammes.
1	6·4806	1·00007
1*a*	6·4796	·99992
2	·6482	·10003
2*a*	·6483	·10004
3	·0655	·01010
3*a*	·0655	·01010
4	·0070	·00108
4*a*	·0071	·00109

With a well-made instrument, the probable error of a specific gravity determination will not exceed 2 or 3 points in the fourth decimal place with a liquid of low viscosity, such as water or even sperm oil, but the viscosities of most lubricating oils at ordinary temperatures oppose so much resistance to the movement of the plummet that the probable error becomes much greater. At sufficiently elevated temperatures the viscosities of oils become so much reduced that the Westphal balance may be used for both oils and fats, provided proper allowance be made for the expansion of the plummet. To determine the sp. gr. of a melted fat at $\frac{100^\circ}{100^\circ}$ C., for example, with an instrument constructed for use at some other temperature, we may proceed in the following manner:—First determine by means of the balance the apparent sp. gr. of water at 100° C.,$=x$, and then the apparent sp. gr. of the oil at 100° C.,$=y$; then $\frac{y}{x}$, with the appropriate correction for vacuo added on (p. 172) is the true sp. gr. of the oil at 100° C. This result × 0·95866 (the density of water at 100° C.) is the density of the oil at $\frac{100^\circ}{4^\circ}$ C. Fig. 56 shows Carter Bell's method of using the balance for determinations at 100° C., D being a glass tube containing the oil or melted fat, C a bath of paraffin wax, and B the water jacket. The tube for the escape of steam should be prolonged upwards well above the beam of the balance. A special plummet may be required, as the thermometer of the ordinary plummet has only a limited range.

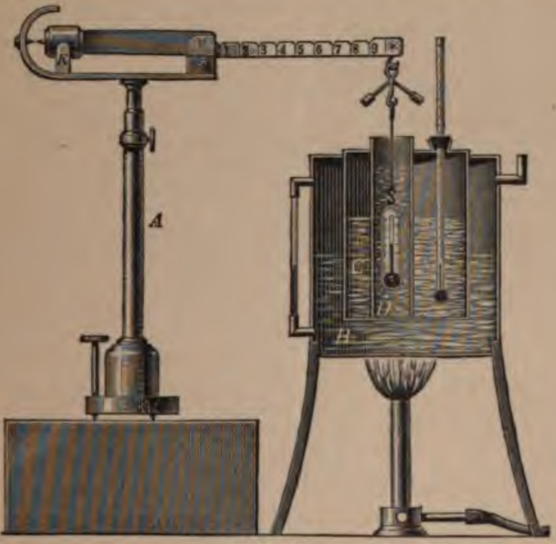

FIG. 56.

Hydrometer Method.—Of all methods for ascertaining the specific gravities of liquids this is the most rapid, and provided the instrument used is correctly graduated, or its error exactly known, very accurate results may be obtained by it with liquids of low viscosity. But no hydrometer can be depended upon unless it has been tested by floating it in two or more liquids of which the specific gravities have been determined by means of [illegible] From the difference, if any, between the true and apparent [illegible] may be constructed for any fairly good instrument [illegible] readings may be corrected. When the viscosity of [illegible] sufficient to impede the free movement of the [illegible] with thick lubricating oils at ordinary temperatures, [illegible] of the method is greatly increased, and in such [illegible] be used where speed is of chief importance [illegible]

[illegible] two classes, viz.—those giving specific gravity [illegible] graduated with arbitrary scales. Hydrometers [illegible] purchased of almost any size and range, and all [illegible] used at the temperature for which they have been [illegible]

[illegible] instruments having arbitrary scales are in use. One [illegible] It is intended for use at 15° C. [illegible] graduated in degrees numbered from 1 to 38, and opposite [illegible] If immersed in rape oil, it [illegible] against which the name rape oil appears; in [illegible] degree; and so on. These numbers [illegible] specific gravities of the oil compared with water = 1·000. [illegible] has a simple scale, but is not much used for [illegible] liquids heavier than water. Degrees, Twaddell [illegible] = specific gravities. Thus 5 deg. Twaddell = 1·025 sp. gr. [illegible] lighter than water an instrument with a [illegible] used, and is converted in the same way. Thus, −5 deg. Twaddell = 1·000 − ·025 = ·975 sp. gr. Table XXXVIII., by Benedikt and [illegible] hydrometers, the temperature at which each [illegible] formula for converting the degrees into specific gravities.

Alcohol Method.—The foregoing methods are not directly applicable to [illegible] first suggested by Fresenius [illegible] This consists in preparing a mixture of [illegible] the solid substance neither sinks nor floats, and [illegible] specific gravity of the liquid. The same method is obviously [illegible] is then conveniently employed for ascertaining the specific gravity of the small quantities of hydrocarbon oil isolated in the process of analysis.

[illegible] substance is being experimented with, it may be prepared for [illegible] recommended by Allen and Chattaway. The fat or wax is melted at the lowest possible temperature and allowed to solidify spontaneously, without artificial chilling, in a flat-bottomed capsule or watch glass. Small fragments are then cut from it with a knife or cork borer. In the case of solid fats which contract greatly on solidification, such as palm-nut and cocoa-nut oils, it is absolutely essential to allow the substance to solidify by standing over night before taking the specific gravity. One of the fragments thus obtained is held under the surface of dilute alcohol, by means of forceps, and carefully freed from adhering air bubbles by means of a camel-hair brush. The specific gravity of the alcohol is then adjusted by adding either stronger or weaker alcohol (not water, because of the air bubbles formed on mixing) until the fragment remains suspended anywhere in the liquid. The specific gravity of the diluted alcohol is then determined by the hydrometer or the Westphal balance. Of course, the final adjustment of the alcohol must be made exactly at the temperature at which the specific gravity of the substance is required to be known.

TABLE XXXVIII.—FORMULÆ FOR CONVERTING HYDROMETER DEGREES TO SPECIFIC GRAVITIES.

Hydrometer.	Temperature.	For Liquids heavier than Water.	For Liquids lighter than Water.
Balling, . . .	17·5° C.	$S=\frac{200}{200-n}$	$S=\frac{200}{200+n}$
Beaumé I., . . .	12·5° C.	$S=\frac{144}{144-n}$	$S=\frac{144}{144+n}$
Beaumé II., . .	15° C.	$S=\frac{144{\cdot}3}{144{\cdot}3-n}$	$S=\frac{144{\cdot}3}{144{\cdot}3+n}$
Beaumé III., . .	17·5° C.	$S=\frac{146{\cdot}78}{146{\cdot}78-n}$	$S=\frac{146{\cdot}78}{146{\cdot}78+n}$
Beck, ...	12·5° C.	$S=\frac{170}{170-n}$	$S=\frac{170}{170+n}$
Brix, ...	12·5° R. 15·625° C.	$S=\frac{400}{400-n}$	$S=\frac{400}{400+n}$
Cartier, . . .	12·5° C.	$S=\frac{136{\cdot}8}{126{\cdot}1-n}$	$S=\frac{136{\cdot}8}{126{\cdot}1+n}$
Fischer, . . .	12·5° R. 15·625° C.	$S=\frac{400}{400-n}$	$S=\frac{400}{400+n}$
Gay-Lussac,* . .	4° C.	$S=\frac{100}{n}$	$S=\frac{100}{n}$
E. G. Greiner, . .	12·5° R. 15·625° C.	$S=\frac{400}{400-n}$	$S=\frac{400}{400+n}$
Stoppani,† . . .	12·5° R. 15·625° C.	$S=\frac{166}{166-n}$	$S=\frac{166}{166+n}$
	C = Centigrade. R = Reaumur.	S = specific gravity (water = 1000). n = degrees.	

* According to Schaedler, ... $S=\frac{100}{100-n}$ $S=\frac{100}{100+n}$.

† ,, ,, ,, ... $S=\frac{160}{160-n}$ $S=\frac{160}{160+n}$.

Reduction to the Vacuum.—The apparent weight of a body in air is less than the true weight by an amount equal to the weight of air displaced by the body. As this is true of the weights as well as of the body weighed, if these happen to be the same in specific gravity, and therefore equal in volume, the error on one side of the scale balances that on the other. But when the body weighed is water and the weights are of brass, about 8·5 times heavier than water, the volumes are nearly as 17 : 2, and therefore the apparent weight of the water is less than the true weight by an amount equal to about $\frac{15}{17}$ths of the weight of air displaced by the water, and the apparent weight of any other liquid equal in volume to the water is short of the true weight by a like amount. Therefore, if W and w be the apparent weights of the water and the liquid respectively, and if $W+x$ be the true weight of the water, then $w+x$ is the true weight of the liquid, and the real specific gravity of the liquid is not $\frac{w}{W}$ but $\frac{w+x}{W+x}$.* x is always very small, and when W and w are nearly the same, *i.e.*, when the specific gravity is near unity, as in the case of most lubricating oils, the error amounts to only one or two points in the fourth decimal place and may be neglected. But in determining the specific gravity of a mixture of glycerol and water for the purpose of ascertaining the viscosity by means of the tables on pp. 134–137, the correction must be applied. As the weight of air varies with the temperature and pressure, the correction is not always exactly the same, but unless an error of ± ·00005 is too great (which is not the case here), the following table † will give the necessary correction without calculation:—

TABLE XXXIX.—CORRECTION FOR REDUCTION OF SPECIFIC GRAVITY TO A VACUUM.

Sp. gr. found.	Correction to be added.	Sp. gr. found.	Correction to be added.
0·75	+ 0·00031	1·05	− 0·00006
0·80	+ 0·00025	1·10	− 0·00012
0·85	+ 0·00018	1·15	− 0·00018
0·90	+ 0·00012	1·20	− 0·00025
0·95	+ 0·00006	1·25	− 0·00031
1·00	± 0·00000	1·30	− 0·00037

Change of Standard. (Determination of Density.)—To reduce the specific gravity of an oil or other liquid, compared with water at $t°$ C. as standard, to the specific gravity compared with water at 4° C. as standard—*i.e.*, to ascertain the *density* of the liquid at $t°$—all that is necessary is to multiply the specific gravity at t° by the density of water at t° which is given in Table XL. on p. 174.*

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* Alder Wright, "On Fluid Specific Gravities," *Jour. Soc. Chem. Ind.*, xi. (1892), p. 297.

† Dittmar, *Chemical Arithmetic*, vol. i. p. 111.

Example.—The sp. gr. of a mixture of glycerol and water at $\frac{20^\circ}{20^\circ}$ C. was found to be 1·1848; therefore the sp. gr. at $\frac{20^\circ}{4^\circ}$ C., *i.e.*, the density of the liquid, is $1·1848 \times 0·99826 = 1·1828$.

Alteration in the Densities of Lubricating Oils produced by Change of Temperature.—In order to determine the viscosity of a lubricating oil at any temperature, it is necessary to know the density of the oil at that temperature. At either 60° F. (15·5° C.) or 212° F. (100° C.) it is easy to determine the density, but at intermediate temperatures it is not always easy. The density may, however, be calculated nearly enough when the densities at 60° F. and 212° F. are known.

In Table XLI. (p. 175) are given the densities at 60° F. and 212° F. of a number of lubricating oils, with the average differences for 1° F. and 1° C. It will be noticed that these differences are very nearly the same for all oils, and it is possible without much error to calculate the density of an oil at any given temperature between 60° F. and 212° F., if we know the density at 60° F., by means of the following formula:—

$$D = d - kt.$$

Where, d = the density of the oil at 60° F.
D = the required density at t° F.

$$k = \begin{cases} 0·000369 \text{ for a fixed oil.} \\ 0·000367 \text{ for a Scotch mineral oil.} \\ 0·000352 \text{ for an American mineral oil.} \\ 0·000350 \text{ for a Russian mineral oil.} \end{cases}$$

The following examples shew the degree of accuracy thus attainable:—

1. *Rape Oil.*

Density at 60° F. (determined) $= 0·9151$

Density at 100° F. (calculated) $= 0·9151 - 0·000369 \times 40 = 0·9003$
Density at 100° F. (determined) $= 0·9002$

Density at 150° F. (calculated) $= 0·9151 - 0·000369 \times 90 = 0·8819$
Density at 150° F. (determined) $= 0·8818$

2. *American Cylinder Oil.*

Density at 60° F. (determined) $= 0·8858$

Density at 100° F. (calculated) $= 0·8858 - 0·000352 \times 40 = 0·8717$
Density at 100° F. (determined) $= 0·8720$

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* Taken from Dittmar's *Chemical Arithmetic*, vol. i. p. 107.

[illegible]	[illegible]	23	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	19	[illegible]
[illegible]	[illegible]	·96149	70
[illegible]	[illegible]	·96079	70
[illegible]	[illegible]	[illegible]	71
[illegible]	[illegible]	·95937	71
100	212	·95866	71

A: 60° F., D=0·99907
70° F., D=0·99803

A: 100° F., D=0·99317
150° F., D=0·98044

TABLE XLI.—TABLE SHEWING THE ALTERATION IN DENSITY OF LUBRICATING OILS CAUSED BY RISE OF TEMPERATURE (*Archbutt*).

DESCRIPTION OF OIL.	DENSITY AT		DIFFERENCE PER ONE DEGREE.	
	60° F. 15·5° C.	212° F. 100° C.	Fahr.	Cent.
Fixed Oils.				
Sperm oil, ...	0·87828	0·82290	0·000364	0·000656
Olive oil, ...	0·91586	0·85962	0·000370	0·000666
Rape oil, ...	0·91506	0·85948	0·000365	0·000659
Tallow, ...	0·87840 at 150° F.	0·85572	0·000366	0·000680
Castor oil, ...	0·96240	0·90500	0·000378	0·000659
		Average,	0·000369	0·000664
Scotch Mineral Oils.				
'865,'	0·86826	0·81160	0·000373	0·000671
'890,'	0·89054	0·83560	0·000361	0·000651
		Average,	0·000367	0·000661
Russian Mineral Oils.				
Refined light machine oil, .	0·89782	0·84420	0·000353	0·000635
„ heavy „ .	0·90960	0·85684	0·000347	0·000625
		Average,	0·000350	0·000630
American Mineral Oils.				
Pale 885/90, ...	0·88436	0·82978	0·000359	0·000647
„ 860/70, ...	0·86766	0·81384	0·000354	0·000638
„ 903/7, ...	0·90082	0·84694	0·000354	0·000638
„ 907/12, ...	0·90540	0·85258	0·000347	0·000626
Red engine oil, 910/20, . .	0·91620	0·86242	0·000354	0·000637
'Bayonne' engine oil, 912/15, .	0·91132	0·85790	0·000351	0·000633
'Globe' oil (dark), . . .	0·88019	0·82726	0·000348	0·000627
Dark med. machinery oil, .	0·88390	0·82910	0·000361	0·000649
'Valvoline' cylinder oil, . .	0·88915	0·83769	0·000338	0·000609
Filtered cylinder oil, 885/90, .	0·88514	0·83058	0·000359	0·000646
„ „ '888,' .	0·88576	0·83505	0·000334	0·000601
Dark A cylinder oil, 890/5, .	0·89908	0·84414	0·000361	0·000651
„ N „ „ 895/900, .	0·89502	0·84175	0·000350	0·000631
„ filtered N, „ '900,' .	0·90230	0·84902	0·000350	0·000631
„ locomotive „ '896,' .	0·89786	0·84414	0·000353	0·000636
		Average,	0·000352	0·000633

[illegible]

[illegible]	[illegible]
[illegible] liver [illegible]	[illegible]
[illegible] free [illegible] tral).	[illegible]
[illegible] oils. Lardine [illegible]	[illegible]
[illegible] to melting point [illegible]	[illegible]

TABLE XLIII.—SPECIFIC GRAVITIES AT $\frac{100^\circ}{100^\circ}$ C. OF SOME MIXED FATTY ACIDS (*Archbutt*).

MIXED FATTY ACIDS FROM :—	SPECIFIC GRAVITY.
Olive oil, ...	0·874 – 0·876
Arachis (earth-nut) oil, ...	0·879
Palm oil, ...	0·870
Rape oil, ...	0·875 – 0·876
Ravison oil, ...	0·880
Cottonseed oil, ...	0·882
Linseed oil, ...	0·892 – 0·893
Poppy seed oil, ...	0·889
Niger seed oil, ...	0·889
Lard oil, ...	0·878
Tallow, ...	0·870
Whale oil, ...	0·892
Blown rape oil (sp. gr. 0·9718), . .	0·923
„ cottonseed oil (sp. gr. 0·9720), .	0·9258

TABLE XLIV.—SPECIFIC GRAVITIES AT $\frac{100^\circ}{100^\circ}$ C. OF SOME MIXED ALCOHOLS (*Archbutt*).

MIXED ALCOHOLS FROM :—	SPECIFIC GRAVITY.
Arctic sperm oil, ...	0·8271
Wool fat, ...	0·9498
Beeswax, ...	0·8239
Carnauba wax, ...	0·8428

TABLE XLV.—SPECIFIC GRAVITIES AT 60° F. (15·5° C.) OF MINERAL LUBRICATING OILS, ROSIN OIL, ETC.

DESCRIPTION.	SPECIFIC GRAVITY.
American pale oils for spindles and light machinery,	·880 to ·895
American pale oils for engines and heavy machinery,	·897 to ·920
American dark machinery oils, chiefly for railroad use,	·877 to ·887
American cylinder oils, ...	·885 to ·905
Russian pale oils for light machinery ('No. 2'),	·895 to ·903
Russian pale oils for heavy machinery ('No. 1'),	·903 to ·910
Russian extra heavy oils, pale and dark, for cylinders and rough machinery,	·902 to ·916
Scotch shale oils (lubricants), ...	·875 to ·895
Rosin oils, ...	·960 to 1·001
Heavy coal tar oils, ...	over 1·010

C.—FLASHING-POINT.

All lubricating oils when sufficiently heated give off vapour. The '*flashing-point*' is the temperature at which the amount of vapour given off is sufficient to form an inflammable or mildly explosive mixture with the air over the surface of the oil, so that on the application of a flame the gaseous mixture ignites and burns with a momentary flash. As the temperature of the oil rises, more vapour is given off, and when the production of vapour is rapid enough to maintain a continuous flame the oil takes fire and burns; the temperature at which this occurs is the 'firing-point,' 'fire-test,' or 'burning-point' of the oil. The determination of these points, more especially of the flashing-point, is of great importance in the examination of lubricating oils, because oils of low flashing-point are unsafe to use.

An important difference exists in the behaviour of the two classes of lubricating oils when heated. The fixed (animal and vegetable) oils do not evaporate, and no vapours are given off (except possibly traces of moisture) on heating them, until the oils begin to decompose; the vapours then given off are products of the destructive distillation of the oil, which requires a fairly high temperature to bring it about, and consequently the flashing-points of such oils are high (over 400° Fahr.). On the other hand, all mineral or hydrocarbon oils evaporate when heated, and the temperature at which sufficient vapour is given off to cause a flash depends upon what hydrocarbons are contained in the oil. Mineral lubricating oils do not as a rule contain the more volatile hydrocarbons of petroleum, which belong properly to the naphtha and burning oil fractions, but '*natural*' oils, and imperfectly refined oils, may give off vapour at temperatures low enough to be dangerous.

Owing to improved methods of manufacture, and greater care in refining, low-flashing mineral oils are more rarely met with than formerly; nevertheless in textile mills, and wherever danger from fire has to be guarded against, the precaution of determining the flashing-point of the lubricating oil must never be neglected. In 1883, Veitch Wilson stated that he had met with one sample of oil offered for lubrication which flashed at the ordinary temperature of the atmosphere, and several which flashed at 150° to 200° F. Prof. Ordway, who examined a large number of oils in actual use in cotton mills in the United States, found several which flashed at 180° F., and a larger number which flashed below 212° F. The use of such dangerous oils would not now be tolerated, and a flashing-point of 340°–350° F. is accepted by oil manufacturers, users, and Insurance Companies, as a standard of safety to which all oils for indoor machinery ought to attain. For outdoor machinery, a limited quantity of oil is still sold having a flashing-point of 200°–210° F.

It is seldom necessary to determine the flashing-points of fixed oils, but, as a means of detecting or confirming adulteration with light mineral oil, the test is sometimes useful.

It is a usual practice to determine the flashing-point of cylinder oils, on the ground that oils of high flashing-point may be expected to evaporate less in the cylinders than those of lower flashing-point. But there is no necessary relation between the flashing-point and the volatility of lubricating oils, and in comparing together mineral oils of different origin (*e.g.*, Russian and American oils) the less volatile oil may even have the lower flashing-point (see Table XLVII. on p. 186). In the authors' opinion, the flashing-point of cylinder oils is a test which might with advantage be dispensed with and replaced by a quantitative determination of the amount lost by evaporation under definite conditions (see Volatility, p. 183).

Determination of the Flashing-Point.

'Open Test.' Flashing- and Firing-Points.—The method formerly used, and still preferred by some, for determining the flashing- and burning-points of lubricating oils, known as the 'open test,' consists in heating some of the oil, in which the bulb of a thermometer is immersed, in a small open metallic cup, a porcelain crucible embedded in sand, or some equivalent contrivance, and passing a small flame across the surface of the oil at frequent intervals. When the amount of vapour given off is enough to form an inflammable mixture with the air, a pale blue flash occurs on application of the test flame, and the temperature at which this flash is first observed is the flashing-point of the oil. To determine the firing-point, the testing is continued until on applying the test flame to the surface of the oil it takes fire and burns continuously.

'Closed Test.'—A little experience is sufficient to shew that the above rough method of determining the flashing-point is incapable of giving uniform results. The temperature at which the first flash is obtained depends upon the presence or absence of air-currents, the rate of heating, the size and shape of the vessel used, the distance of the test-flame from the oil surface, etc. The authors were among the first to abandon the 'open' in favour of the 'closed test,' now almost universally employed for testing lubricating as well as burning oils. For this purpose a brass cup furnished with a close-fitting lid and slide (an exact copy of the Abel petroleum cup) was constructed with brazed joints, so as to stand heating to a high temperature, and instead of the outer water-bath a thick cast-iron cup on feet was made in which the test-cup fitted loosely. Heat was so applied to the cast-iron body as to cause the temperature of the oil to rise rapidly at first, and when near the flashing-point the rate of heating was reduced to about two degrees per minute, and the gas testing flame was applied every two degrees by opening the slide, exactly as in the Abel test. Improved forms of apparatus have since been devised by Pensky and Martens, and by Gray, in which the important addition of a stirrer has been introduced, which enables the heating of the oil to be conducted much more rapidly without impairing the uniformity of the results.

The Pensky-Martens Test Apparatus.—This apparatus, shewn in fig. 57, consists of the brass cup A with flange B, which drops loosely into the cast-iron body C, the flange resting upon the dome-shaped brass shield D.

[illegible] which engage in slots in the [illegible] a revolving perforated slide [illegible] which the openings in the [illegible] openings in the lid, and the little gas [illegible] through the central opening [illegible] the mixture of air and [illegible]. The lid also carries the stirrer [illegible] the air space; also [illegible]

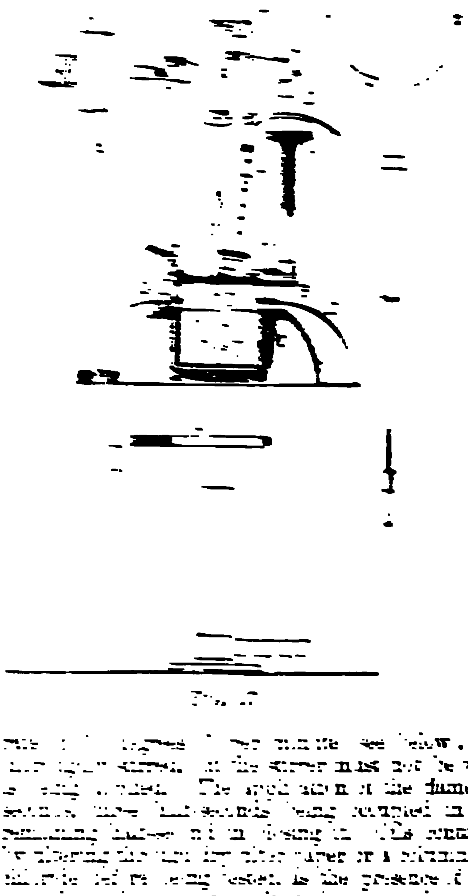

Fig. [illegible]

In making a test, the cup is placed upon a level surface and filled with oil to the mark. It is then placed in the test-apparatus, and the lid is put on. The small test flame having been lighted and turned down until the luminosity has almost disappeared, the oil is gradually heated by means of the burner B, the wire net L being swung out of the way. The flame at first used is large enough to heat the oil rapidly, but as soon as the test flame when lowered into the cup shows a tendency to enlarge, the heat is moderated and the wire net may be swung over the flame. The stirrer is now worked so as to keep the oil as well as the vapour and air thoroughly mixed, and the test flame is applied at every two degrees rise of temperature until the flashing-point is reached. The temperature of the oil towards the end of the experiment may rise at the rate of [illegible] degrees [illegible] per minute (see below), so long as the oil is kept [illegible] stirred, but the stirrer must not be worked while the test flame is being applied. The application of the flame should occupy about two seconds, [illegible] seconds being occupied in opening the slide and the remaining [illegible] in closing it. [illegible] remaining water must be dried by filtering the oil through filter paper or a column of coarsely-crushed calcium chloride before being tested, as the presence of much moisture causes very irregular and incorrect results to be obtained.

This apparatus has been subjected to an elaborate series of tests by Holde. By making repeated tests with oils of different flashing-points, he has shewn that rapid heating with continuous vigorous stirring gives the same results as slow heating without stirring, and when testing the same oil several times the results agreed within 2 or 3 degrees C. (3⅗° to 5⅖° F.) even when the thermometer rose as rapidly as 10° C. (=18° F.) per minute towards the end of the experiment. According to Holde, a rise in temperature of 12° C. (=22° Fahr.) per minute is permissible. The size of the testing flame does not influence the result appreciably, but it is not desirable to use too large a flame, otherwise the flash may not be plainly seen. Filling the oil holder above the mark, and so reducing the air space, tends to lower the flashing-point. Thus Holde found, that with an oil flashing at about 155° C. (=311° F.) the mean flashing-point differed 4° C. (=7·2° F.) according to whether the cup was filled 1 cm. below or 1 cm. above the mark. Accordingly it has been proposed by Aisinmann* that as an oil of high flashing-point will expand during the test more than an oil of low flashing-point, the cup should not be filled to the same mark with all oils, but the quantity used should be such as will by expansion have reached to the mark at the flashing-point. Thus, taking 0·00068 (per 1° C.) as the coefficient of expansion of Russian lubricating oils, the total expansion per 75 c.c. of oil (the quantity used in the Martens cup) is 0·5 c.c. per 10° C. Therefore, the quantity of oil to be used in order to ascertain the correct flashing-point of an oil flashing at say 200° C. should be, according to Aisinmann, not 75 c.c., but (at an initial temperature of 20° C.)—

$$75-\left(\frac{200-20}{10}\right)\times 0{\cdot}5=66 \text{ c.c.}$$

Correcting the volume in this way Aisinmann obtained the following results:—

Table XLVI.

Usual Volume.	Corrected Volume.			Difference °C.	Reduction in Volume of Oil used. c.c.
Flashing Point °C.					
151°	153°	154°	...	2·5°	6·55
193°	200°	200°	...	7·0°	8·65
257°	266°	268°	268°	10·3°	11·85

To adopt Aisinmann's proposal would greatly increase the labour of determining the flashing-point, without any equivalent advantage. The test, however performed, is an empirical one, and all that is required is the adoption of a uniform system of testing, so that disputes between manufacturers and users may be avoided. The principal object of determining the flashing-point is the detection of dangerous and wastefully volatile oils, and from this point of view the method of testing which gives the lowest result is to be preferred.

Holde † has since published further experiments shewing that with oils flashing between 172° and 241° C. (342° and 466° F.) a variation of even as much as 13 c.c. below the normal filling of the cup does not alter the flashing-point more than 1°-1·5° C. (1·8°-2·7° F.).

Gray's Test Apparatus.—This (fig. 58) is an adaptation of the Pensky-Martens revolving slide and stirrer to the Abel cup. The inventor states ‡

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* *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 284.

† *Ibid.*, xvi. (1897), p. 322. ‡ *Ibid.*, x. (1891), p. 348.

Fig. [illegible].—[illegible] [illegible] are three orifices, one, at which the test light is applied, the other two, situated one at either side of it, being for the admission of air. It will thus be readily seen that the change from stirring to testing and vice versa can be instantly performed.

"The results obtained by this apparatus are identical with those obtained by the Pensky-Martens. They are not affected by the source of heat, a naked flame giving the same results as the sand bath. It is immaterial what the rate of heating is, provided it is not too rapid to prevent a correct reading of the thermometer. I prefer to reduce the rate of heating when nearing the point at which the oil is expected to flash. The stirrers do not require to be worked continuously, but merely at intervals. I find it advisable to stir more frequently when the rate of heating is fast."

D.—VOLATILITY.

The property of being volatile or capable of evaporating without decomposition distinguishes the hydrocarbon oils from the fixed oils, but the temperature at which evaporation takes place depends upon the nature of the hydrocarbons contained in the oil. In any case the oil does not evaporate unchanged, for those hydrocarbons which are most volatile pass off first, leaving the less volatile hydrocarbons as a more or less viscid residue.* If the oil be a mixed one, the fatty component remains also, and the composition and character of the original oil may thus become entirely changed. The best qualities of machine oil scarcely evaporate in use, but at the high working temperatures of steam cylinders all mineral lubricating oils evaporate. It is obvious that an oil which evaporates to a serious extent at the working temperature cannot be an economical lubricant, since all that evaporates is lost and the remainder may form a viscid or even a dry residue on the bearing. Notwithstanding its importance, this property of lubricating oils seldom receives the attention it deserves, a high flashing-point being generally regarded as sufficient evidence of the durability of even cylinder oil. Veitch Wilson long ago called attention to this anomaly, pointing out that the significance attached to the flashing-point should be limited to what it really indicates, viz. :—the relative safety of an oil, whilst the tendency to evaporate should be ascertained by measuring the actual loss of weight under definite conditions of time and temperature.

Determination of Volatility.—The usual method of determining the volatility of mineral lubricating oil is to place a weighed quantity, 0·5–1·0 grm., in a shallow dish or watch glass and expose it in a water- or air-oven for a certain number of hours, noting the loss of weight. Veitch Wilson states that machine oils when exposed in this manner for 10 hours at the temperature of the ordinary water-oven (about 212° F.) should not lose weight, whilst Hurst states that the loss in 24 hours should not exceed 0·25 to 0·5 per cent. Cylinder

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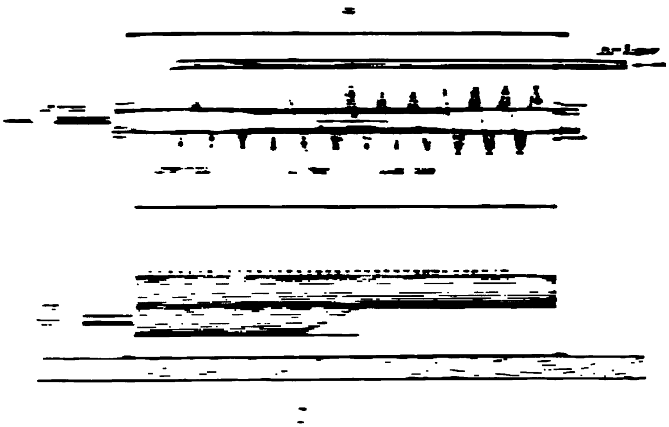
* At temperatures above 200° C. the heavy hydrocarbons decompose.

[illegible]



[illegible]

The current of air is maintained at the constant speed of 2 litres per e by means of the simple regulator shewn in fig. 60. The air enters gulator at A, and a slight excess is kept continually escaping at the end of the wide tube B which is immersed to the depth of 3 inches in The supply is taken from the branch C, the orifice of which is d until just large enough to pass 2 litres per minute against atmos- pressure under the 3 inches head of water.*

quantity of oil used for a test is 0·5 grm., which forms a thin layer e bottom of the platinum nd the oil is exposed to the rent for exactly 1 hour. emperature of the oven is to suit the requirements of st. For cylinders working lbs. pressure per sq. in., the ested at 370° F., and should se more than from 0·5 to 1 nt. in weight in the time ed (1 hour).

t be desired to use a cur- f steam instead of air, the end of the vaporimeter is ted to a flask or boiler, he outlet to a condenser. gas flame under the boiler gulated so as to distil a e quantity of water in the 100 c.c. being a convenient e, though 92 c.c. is the volume ed to give a current of steam equal to the above men- air current. The boiler is ed, all the steam is blown the tube, and the platinum ontaining the oil is inserted. waiting a few minutes for ay of oil to become heated e steam current is turned f the tray be inserted with- rst blowing out the steam, condenses upon the tray, the eps over the edge, and the spoiled.

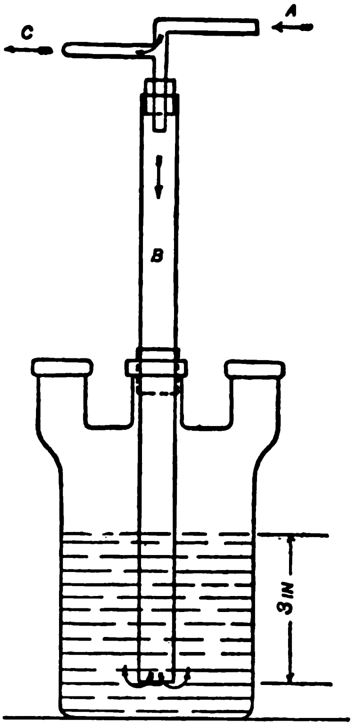


FIG. 60.

e figures in the following table shew the kind of results obtained is test. All the samples of oil tested were pure mineral oils, the hree being described as cylinder oils, and the last two as ne oils.

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is is done by connecting the exit-tube C, by means of a flexible tube and o the neck of a bell-jar of known capacity, full of water, sunk in a bucket r. As the air passes into the bell-jar, the latter is gradually raised so as ntain the same water level within and without the jar, and the orifice of anch C is made of such dimensions as will allow the jar to fill in the ted time.

TABLE XLVII.—FLASHING-POINTS AND VOLATILITY COMPARED.

No.	Description.	Sp. Gr. at 60° F.	Flashing-Point (Pensky-Martens) ° F.	Loss of Weight in 1 hr. at 370° F.	
				In Air; 2 Litres per Minute.	In Steam; 100 c.c. of Water condensed per hour.
				Per cent.	Per cent.
1	American cylinder oil, . .	0·902	585°	0·12	...
2	" " " .	0·898	512°	0·54 0·56	0·70 0·46 0·68
3	" " " .	0·893	424°	4·18	...
4	American machine oil, .	0·897	402°	16·8 16·3	18·1 17·6
5	Russian machine oil, . .	0·909	380°	14·7 14·3	16·0 16·7

As the volume of steam passed over the oils in these experiments was about 8 per cent. in excess of the volume of air, the figures in the two last columns are not comparable. But if we assume the rate of evaporation to have been proportional to the volume of steam, and correct the results accordingly, the following numbers are obtained, which agree so closely as to shew that the rate of evaporation in both steam and air is the same.

Average Loss per cent.	No. 2.	No. 4.	No. 5.
In air current, ...	0·55	16·55	14·50
In steam current of same volume (calculated), ...	0·57	16·32	15·04

It is evident that no simple relation exists between the volatility of an oil and the flashing-point. It is true of the four American oils that as the flashing-point falls the volatility increases; but the Russian oil flashing at 380° lost less by evaporation than the American oil flashing at 402°. The two oils flashing at over 500° F. both lost less than 0·6 per cent., though there is a difference of 73° F. in their flashing-points, on the other hand, No. 3, which flashed 88° F. below No. 2, lost over 4 per cent., and No. 4, which flashed at only 22° F. lower still, lost over 16 per cent.

E.—SETTING-POINT OR COLD TEST OF LUBRICATING OILS.

The effect of cold upon lubricating oils is not the same as upon simple fluids such as water, glycerin, etc. The latter have fixed and accurately ascertainable freezing-points, at which a complete change from the liquid to the solid state takes place, but lubricating oils, which are mixtures of bodies of various melting-points, behave like solutions, and frequently deposit some portion of their constituents before the whole mixture solidifies. Thus, olive and lard oils deposit a solid fat, sperm oil deposits spermaceti, and some hydrocarbon oils deposit paraffin. The 'setting-point' of an oil will therefore vary according to whether it be regarded as the temperature at which solid matter commences to separate, or the temperature at which the oil completely loses its fluidity. The setting-point of Scotch mineral oils is considered to be the temperature at which the separation of solid paraffin is observed to commence; but Russian oils, some pale American oils of high viscosity, and all dark-coloured or opaque oils, which either deposit no paraffin or in which the separation cannot be seen, are considered to have reached their setting-point when they cease to flow. The low setting-point of Russian lubricating oils, which deposit little or no paraffin, is characteristic, and serves to distinguish them from the American and Scotch oils; Russian oils, when cooled, simply become more and more viscous until the setting-point is reached. Among vegetable lubricating oils, castor and almond oils have the lowest solidifying-points.

Very erroneous conclusions regarding the setting-point of an oil may be formed unless sufficient *time* be allowed in making the test. This is especially true of fixed oils. Thus, Salkowsky [*] found that a cod-liver oil, which remained perfectly clear when cooled for a short time to − 15° C., became quite solid after several hours' exposure to − 4° C. The subject has been more fully investigated by Holde.[†] The solidification of such oils is promoted by stirring, and by adding to the fluid oil a fragment of the same oil in a frozen state. Mineral oils assume their permanent state for any given temperature much more rapidly than the fixed oils, and, except when testing by the Scotch method (see below), they should not be stirred, as the network of solid hydrocarbons, which sometimes causes such oils to set before they have wholly solidified, is broken up by the stirring and the setting-point is thereby lowered. Mineral lubricating oils frequently undergo a change in their solidifying points by previous heating, and it is therefore important that the portion used for the setting-point determination should not have been recently used for any other test which has involved heating above the atmospheric temperature.

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[*] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 37.

[†] *Ibid.*, ix. (1890), p. 112; also xv. (1896), pp. 138 and 160.

Determination of the Setting-Point.—**The Scotch Method** for ascertaining the temperature at which a mineral oil commences to deposit paraffin is as follows*:—The oil is poured to the depth of about 2 inches into a thick-walled test-tube about 1¼ inches in diameter, and the tube is immersed in a freezing mixture and slowly stirred by a thermometer until it has been cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing-mixture, wiped, and held up between the eye and a window, and, whilst the oil is constantly stirred with the thermometer, the temperature at which the last trace of solid paraffin disappears is read off. This operation is repeated with the same sample of oil until two experiments give concordant results, and the temperature so found is the setting-point of the sample.

Archbutt's Method for determining, approximately, the temperature at which an oil ceases to flow is carried out in a refrigerator (fig. 61), consisting

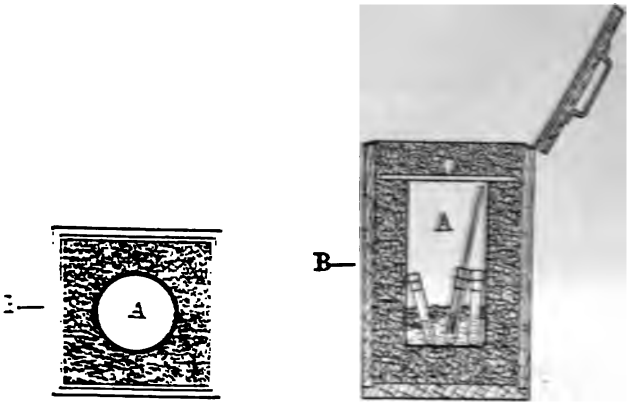

FIG. 61.

[illegible] leaden jar A, 6 inches in diameter and 14 inches in depth, [illegible] contained in a wooden box B, measuring 12 inches [illegible] inches deep. The space between the leaden jar and [illegible] cotton waste; 3 inches of waste are placed below [illegible] the jar is covered by a loose wooden lid on which [illegible] waste is placed. The box has a hinged lid. The oils to be [illegible] depth of about 2 inches into glass specimen tubes [illegible] length by about ⅝-inch in internal diameter, and [illegible] A similar tube containing Russian lubricating oil [illegible] setting-point is used to contain the thermometer, which [illegible] jar standing in the rack and has its bulb immersed in [illegible]

[illegible] crushed ice having been placed in the jar, the [illegible] in the ice and left there for at least one hour. [illegible] examined, and any oils which will [illegible] held in a horizontal position and lightly tapped [illegible] as having set in ice, or are placed aside for further experiment. The remainder are returned to the ice after this has been mixed, by thorough stirring, with sufficient powdered salt to lower the temperature about 5° F. The quantity to add is soon learned by experience. After 20 minutes' exposure to the lower temperature the tubes are again examined, any oils which have now set are taken out and the temperature is read off on the thermometer. The addition of salt is repeated, and the gradual lowering of temperature with examination of the oils every 20 minutes is continued until the last oil has set, or until the temperature can be reduced no further. In this way the setting-point of an oil is ascertained within 5° F. A closer approximation can be made, if desired, by a second experiment, in which the temperature, when near the setting-point, is more gradually lowered. The setting-points of oils which solidify at temperatures above that of melting ice may be ascertained by placing the tubes in water at the temperature of the laboratory, and then gradually lowering the temperature of this water by the addition of small quantities of ice until the setting-point of the oil has been reached. Animal and vegetable oils must be stirred frequently, and the lowering of the temperature must be more gradual than in the case of mineral oils.

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* [illegible] Soc. Chem. Ind. x. [illegible] 347.

Hofmeister's Method.—The special feature of this method is the use as freezing liquids of saline solutions of such strength that they are saturated at their freezing-points; such solutions when partially frozen remain constant in temperature until they have become entirely liquefied or solidified, and are thus very convenient for keeping the temperature of an oil constant for a length of time. The following solutions may be used:—

TABLE XLVIII.—SALINE FREEZING SOLUTIONS.

Salt.	Parts of Salt per 100 parts of water.	Freezing Point of the Solution.	
		Fahr.	Cent.
Potassium sulphate,	10	28·6°	- 1·9°
Sodium carbonate crystals,	20	28·4°	- 2·0°
Potassium nitrate,	13	26·9°	- 2·85°
Potassium nitrate,	13	23·0°	- 5·0°
Sodium chloride,	3·3		
Barium chloride,	35·8	16·3°	- 8·7°
Potassium chloride,	30	12·4°	-10·9°
Ammonium chloride,	25	4·3°	-15·4°
Ammonium nitrate,	45	1·85°	-16·75°
Sodium nitrate,	50	0·05°	-17·75°
Sodium chloride,	33	-4·3°	-21·30°

A solution selected from the above list is placed in the vessel *a* (fig. 62), and about 4 c.c. of the oil to be tested are placed in one of the tubes *h* immersed in the solution. A freezing-mixture of ice and salt is placed in the outer vessel *b*. As soon as the temperature of the solution in *a* has fallen to its freezing-point, if it does not commence to crystallize it is caused to do so by stirring, or by dropping in a small portion of the same solution which has been previously frozen in a test-tube. The temperature of the liquid in *a*, and therefore of the oils in tubes *hh*, will now remain constant so long as the liquid remains only partially frozen, and to maintain it in this condition and prevent complete solidification from taking place, all that is necessary is to lift the vessel *a* out of the freezing mixture occasionally for a few minutes. After the lapse of 1 or 2 hours, the tubes of oil are lifted out of the bath, and any oils which do not flow on inclining the tubes are considered to have set at the temperature of the bath. The remainder are then tested in a solution freezing at a lower temperature. The standard liquids are preserved for use in stoppered bottles. This is a scientific method for determining accurately the effect on oils of prolonged exposure at low temperatures.

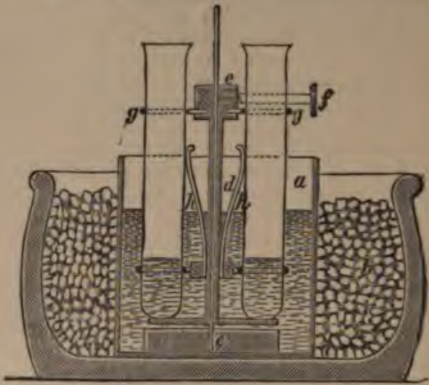

FIG. 62.

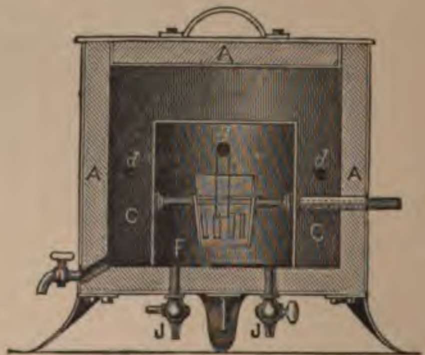

FIG. 63.

Schultz's Method.—In this method, used in Germany, the oil is cooled until of such consistency that when subjected to a fixed pressure in a tube of specified diameter it will flow at a definite minimum speed. The oil to be tested is introduced into a glass U-tube, 6 mm. in internal diameter, which is filled to a depth of 30 cm. in each limb. Several such tubes, supported by a suitable stand, may be cooled together in a solution of known freezing-point, Hofmeister's method, the time of cooling being 1 hour. Each tube cession is then connected by its longer limb with a manometer, and by ng a pinchcock a pressure equal to 50 mm. of water is caused to act the oil. The specification of the Prussian State Railways stipulates he oil when thus tested after cooling for 1 hour at a temperature of C. in winter or − 5° C. in summer must flow in the tube at a minimum f 10 mm. per minute.

gliabue's Standard Oil Freezer (fig. 63), used in the United States, is ircular in shape with a flat side. It consists of an inner chamber F, unded by an ice-chamber C, with a non-conducting jacket A, filled with os. The oil is contained in a glass cup, 4 inches in depth and 3 inches meter, which is fixed upon a rocking shaft by means of which the cup e tilted and the condition of the oil seen. A thermometer is immersed oil, and two others register the temperature of the ice chamber. Two ocks connected to the inner chamber are for the introduction of warm f it is desired to raise the temperature, and the tap at the side is for ing away the liquefied ice. A glass window in the flat side enables the be observed.

TABLE XLIX.—SETTING-POINTS OF SOME VEGETABLE AND ANIMAL OILS.

OIL.	Setting-Points.	
	° F.	° C.
chis (earthnut) oil, .	+32 to +19·4	0 to −7
ch nut oil, . .	+ 1·4	−17
ıeline oil, . .	− 0·4	−18
or oil, . . .	+14 to −0·4	−10 to −18
liver oil, . .	+32 to +14	0 to −10
onseed oil, . .	+33·8 to +50	+ 1 to +10
cas oil, . . .	+37·4	+ 3
npseed oil, . .	Between +5 and −17·5	Between −15 and −27·5
d oil, . . .	+25 to +42	−4 to −5·5
seed oil, . . .	Between +5 and −17·5	Between −15 and −27·5
ze oil, . . .	+14 to −4	−10 to −20
tard oil (black), .	+23 (*Holde*) +0·5 (*Chateau*)	−5 (*Holde*) −17·5 (*Chateau*)
,, (white), .	+17·6 to +3·2	−8 to −16
tsfoot oil, . .	+32 to +50	0 to +10
erseed oil, . .	Below +15·8	Below −9
e oil, . . .	+39·2 to +21·2	+ 4 to −6
pyseed oil, . .	+ 3·2 to − 1·3	−16 to −18·5
poise oil, . .	+ 3·2	−16
e oil, . . .	+28·4 to +10·4	− 2 to −12
oil, . . .	+28·4 to +26·6	− 2 to −3
mé oil, . . .	+24·8 to +21·2	− 4 to −6
rm oil (Southern ıd Arctic), . .	About 32°	About 0°
flower oil, . .	+ 3·2 to −1·3	−16 to −18·5
nut oil, . . .	Between +5 and −17·5	Between −15 and −27·5

TABLE L.—SETTING-POINTS OF MINERAL LUBRICATING OILS.

Description.	Setting-Point.
Scotch Oils, .	About 32° F. (*Veitch Wilson*).
American Oils,	Very variable. Depends largely upon the amount of solid hydro-carbons present. Winter machinery oil generally sets at 25° to 32° F. (−4° to 0° C.) by Archbutt's method; but oils which do not set above 15° F. (−9° C.) are met with.
Russian Oils, .	The best qualities of refined machine oil do not cease to flow when cooled to zero Fahr. (−18° C.).

F.—MELTING-POINTS OF FATS AND LUBRICATING GREASES.

Melting and Solidifying Points of Fatty Acids.—In the melting of natural fats, mixed fatty acids, lubricating greases, etc., the same phenomena present themselves as are observed in the setting or solidifying of oils, viz.:—that, as we are dealing with mixtures, the temperature of incipient fusion, at which some portion of the substance becomes fluid, and the temperature of complete fusion, at which the whole has liquefied, are not, as a rule, the same. It has also been observed that the melting-points of fats and fatty acids may be profoundly modified by previous heating of the melted substance. Thus Clague * found that the melting-point of cacao-butter, originally 75° F., was raised to 86° F., by keeping the melted fat at a temperature just under 100° F. for 2 hours. A temporary change in the melting-point usually occurs immediately after the substance has been melted and re-solidified. Thus Bevan † found that a crystallized fat obtained from lard, which had been melted in a test-tube and then caused to solidify rapidly by chilling in cold water, re-melted at a temperature about 15° below the first melting-point; on gradually raising the temperature, the fat re-solidified and regained its normal melting-point. In consequence of such facts as the above, the temperatures recorded as the melting-points of fats and fatty acids by different observers, using different methods of preparation and manipulation, unfortunately present discrepancies which will not be removed until some uniform system of testing has been agreed upon.

In the examination of lubricants, the object of a melting-point determination may be twofold. Firstly, a knowledge of the melting-point of a fat or lubricating grease may be required for the purpose of ascertaining its behaviour under the practical conditions of lubrication; and secondly, the melting- or solidifying-point of a fatty acid or of a mixture of fatty acids may be required as a means of identifying the oil or fat from which the fatty acid or mixture has been obtained.

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* Allen, *Coml. Org. Anal.*, vol. iii. pt. ii. p. 570.

† *Analyst*, xviii. (1893), p. 286.

Preparation of the Substance.—Whatever method be employed, certain precautions must be observed in the preparation of the substance, chief of which are the following:—

(1) Except in the case of lubricating greases ('solidified oils') every trace of moisture present must be removed. Having melted the substance in the water-oven and allowed all visible water to settle out, the fat or oil is poured off, and the remaining traces of moisture are got rid of either by filtering through dry filter paper or by further heating in the water-oven until a cold glass placed over the beaker no longer becomes dimmed by condensed water vapour. Lubricating greases, in which water may be present as an essential constituent, must of course be tested without any previous preparation.

(2) In melting fats or fatty acids, previous to the determination of the melting-point, the temperature should not be raised higher, and the heating should not be continued longer, than is absolutely necessary.

(3) Sudden chilling to hasten re-solidification must not be resorted to. The substance must be allowed to solidify naturally. If the temperature of the room be above the solidifying-point, the substance should be placed in a sufficiently cool cupboard or refrigerator, and after solidification has taken place, at least an hour or two, and in most cases from 12 to 24 hours, should be allowed to elapse before the determination of the melting-point is undertaken.

Determination of Melting- and Solidifying-Points.—Pohl's Method.—By this method the temperature of incipient fusion, at which a substance begins to melt, is determined. The bulb of a thermometer T (fig. 64) is dipped into the melted substance and removed with a coating of the substance adhering to it. After this has solidified, and has remained for a sufficient length of time to acquire its normal melting-point, the thermometer is fixed, by means of a cork, in a long boiling-tube C, the bulb of the thermometer being placed about ½ inch above the bottom of the tube. A groove is cut in the side of the cork for the escape of air. The tube is then supported in the clamp of a retort stand, about 1 inch above a disc of sheet iron or asbestos, which is heated by means of a small flame so that the temperature rises very gradually. The moment a drop of liquefied fat is observed to collect at the lower part of the thermometer bulb, the temperature is read off and is recorded as the melting-point. This is a very good method for the examination of tallow and other fats.

Stock's Method for Greases.—The following modification of Pohl's method has been recommended by Stock for ascertaining the melting-points of soap-thickened oils.* A clean, narrow test-tube is fitted over the lower end of a thermometer, by means of a band of stout indiarubber tubing, the annular space between the walls of the tube and the thermometer not exceeding one-sixteenth of an inch. The narrow test-tube is fixed, by means of a cork, within a wider and longer tube. A small quantity of the sample to be tested is taken upon the bulb of the thermometer, which is then carefully inserted into the inner tube, down to within half an inch of the bottom. The wider tube is then immersed in a beaker of either water or clear lard oil (according to the melting-point of the grease) and is heated on a disc of asbestos millboard supported over a Fletcher's Argand-Bunsen. By bringing the tube up to the side of the beaker, the temperature at which the mass flows down to a clear bead at the bottom of the tube may be observed, by means of a hand-lens if necessary. This is recorded as the melting-point of the sample.

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* *Analyst*, xiv. (1889), p. 2.

Capillary Tube Method.—This simple method for determining the point of incipient fusion is frequently used for the examination of fatty acids and other substances of fairly definite, and not too low, melting-point. There are several ways of operating, but the following is one of the most convenient. The capillary tubes, which are made by drawing out soft glass tubing, should be very thin-walled, about 10 cm. long and 1 mm. in internal diameter. They are left open at both ends. One end is dipped into the melted substance, until enough has risen to fill about 1 centimetre of the tube, which is then laid aside in a cool place for several hours, preferably over night, for the substance to solidify and regain its normal melting-point. The other end of the tube is then held for a moment in a small flame and, while hot, is pressed against a small bar of wood W, fig. 65, coated with sealing wax, by which means four or more of such tubes may be supported in a beaker of water as shewn in the sketch. The beaker is placed upon a disc of asbestos millboard over a burner, and a thermometer T, held by a clamp or suspended by a cord, is placed with its bulb close to the filled ends of the capillary tubes. The water in the beaker is then slowly warmed up and continually stirred by the glass stirrer S, and the temperatures at which the substances melt and rise up the capillary tubes are recorded. The mean of two experiments in separate tubes, which should closely agree, is taken as the melting-point of the

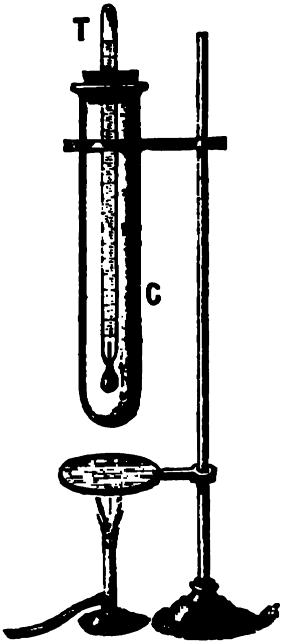

FIG. 64.

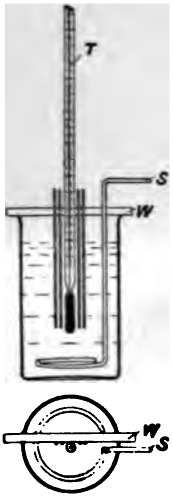

FIG. 65.

substance. In examining mixed fatty acids, it is frequently noticed that a portion will liquefy and run up the tube, leaving the remainder still solid behind. Clague found that the melting-point of cacao-butter determined in a capillary tube varied according to the diameter of the tube.

Bensemann's Method,* which is preferable to the above, determines two points, viz.—the temperature of incipient fusion and the temperature of complete fusion. A piece of narrow thin-walled tubing is drawn out to a capillary point and sealed at the small end. A small portion of the substance is then melted in the wider portion of the tube, in the position shewn at *A a* (fig. 66) and is allowed to solidify. After a sufficient interval the tube is attached, by means of two small indiarubber rings cut off a piece of tubing, to a thermometer, with the fat close to the bulb, and the thermometer is supported vertically in a beaker of water. The water is slowly warmed up, with continual stirring, until some of the fat begins to flow; the temperature observed at this moment is the '*point of incipient fusion*.' When the substance has melted to a perfectly clear and transparent liquid, as shewn at *b* (fig. 66), the temperature is again read off and is the '*point of complete fusion*.'

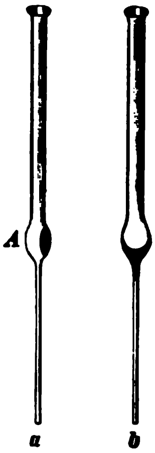

FIG. 66.

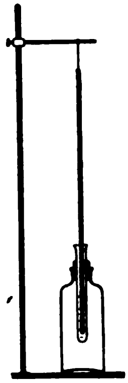

FIG. 67.

Bach's Method.—Bach and Hübl have published a number of melting- and solidifying-points of fatty acids which were ascertained in the following way. The substance was brought into a test-tube about 7 mm. in diameter, and whilst being stirred gently with a thermometer, the temperature was noted at which the mass became quite clear ('*melting-point*'), and that at which a cloudiness began to form ('*solidifying-point*').

Cook's Method.†—This is a modification of T. Redwood's method.‡ Two beakers are supported one within the other, the minimum space between them being 1 inch at the sides and 1½ inches at the bottom. About 1 inch in depth of mercury is placed in the inner beaker. The outer beaker contains either water or melted paraffin (according to the temperature required) the surface of which must be at least 3 inches above the surface of the mercury. Minute fragments of the substance whose melting-point it is desired to determine are placed on a small piece of ferrotype-plate (with the varnish removed), or on a microscope cover-glass, and floated on the surface of the mercury, in which the bulb of a thermometer is immersed. The beaker is covered with a card. The water or paraffin in the outer beaker is then slowly heated up with frequent stirring, until the substance is observed to melt; it is then allowed to cool and the solidifying-point may be read off. This method is said to give closely concordant results.

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* *Jour. Soc. Chem. Ind.*, iv. (1885), p. 535.

† *Proc. Chem. Soc.*, xiii. (1897), p. 74.

‡ *Analyst*, i. (1877), p. 51.

TABLE LI.—MELTING-POINTS OF SOME FATS, WAXES, ETC.

DESCRIPTION.	NAME.	MELTING-POINTS.	
		° F.	° C.
Fats.	Bone fat, ...	69·8– 71·6	21–22
	Coconut oil, . . .	68·0– 82·4	20–28
	Cotton seed stearin, . .	78·8–104	26–40
	Horse fat, . . .	107·6–109·4	42–43
	Lard, ...	96·8–118·4	36–48
	Palm oil, ...	80·6–108·5	27–42·5
	Palm nut oil, . . .	73·4– 82·4	23–28
	Tallow (beef), . . .	107·6–119·3	42–48·5
	„ (mutton), . .	111·2–123·8	44–51
Waxes.	Beeswax, ...	142·7–158	61·5–70
	Carnauba wax, . . .	181·4–186·8	83–86
	Spermaceti, . . .	109·4–113	43–45
	Wool fat (neutral), . .	87·8–108·5	31–42·5
Hydrocarbons.	Cerasin (refined ozokerit), .	141·8–172·4	61–78
	Paraffin wax, . . .	98–137	36·7–58·3
	Vaseline, ...	104–122	40–50

Dalican's 'Titre Test.'—This test, which was devised by Dalican for the valuation of tallow by determining the solidifying-point of the mixed fatty acids, has been applied by Lewkowitsch to a large number of oils and fats. The fatty acids, obtained from 100 grms. of fat by the method described on p. 227, perfectly dried by filtration through paper in the water-oven and allowed to solidify over night, are re-melted at as low a temperature as possible and introduced into a stout-walled test-tube, measuring 7 inches long by 1⅜ inches diameter, which is filled rather more than half-full. The tube is supported, by means of a cork or a rubber ring, in a wide-mouthed bottle of colourless glass (see fig. 67), and a centigrade thermometer, graduated, say from 0° to 70°, in fifths of a degree, is suspended with its bulb in the centre of the fatty acids. As soon as crystals begin to appear at the bottom of the tube the fatty acids are stirred by giving the thermometer a rotatory movement, first thrice to the right, then thrice to the left, and then continuously in one direction, without touching the sides of the tube, but taking care that the whole mass is kept uniformly mixed. When the mixture becomes turbid

TABLE LII.—MELTING- AND SOLIDIFYING-POINTS OF MIXED FATTY ACIDS.

LASS.	MIXED FATTY ACIDS FROM	MELTING-POINTS ° C.			SOLIDIFYING-POINTS ° C.	
		Bensemann's Method.		Other Methods.	Various Methods.	'Titre' Tests (*Lewkowitsch*).
		Point of Incipient Fusion.	Point of Complete Fusion.			
getable n-drying ils and fats.	Olive oil,	23–24	26–27	24–27* 19–28·5†	17–24·6	17·15–26·4 (12 samples)
	Arachis (earthnut) oil,	31–32	34–35	27–33	22–31	29·2
	Castor oil,	..	..	13	2–3	..
	Palm oil,	..	..	41–50	39–46·2	35·9 –45·5
	Palm nut oil,	..	..	20·7–28·5	..	20·5 –25·5
	Coconut oil,	..	..	24–27	15·7–20·4	22·5 –25·2
	Japan wax,	..	..	56–57	53–56·5	59·4
	Cotton seed stearin,	..	..	27–30	21–23	35·1
getable ni-drying oils.	Rape oil,	18–19	21–22	16-21	10·5-18·5	12·2 -13·6
	Rape oil, (Stettin),	..	..	..	..	18·5 (*Archbutt*)
	Ravison oil	..	..	..	..	below 0° (,,)
	Mustard oil,	..	..	15–17	15·5	..
	Cottonseed oil,	39–40	42–43	34–40	30·5–36	37·6
	Cottonseed oil,	..	..	..	..	32·7–35·2, part of the stearin removed
	Curcas oil,	..	..	27·5	..	28·6
	Sesamé oil,	25–26	29–30	21–32	18·5–28·5	22·9 -23·8
	Beech nut oil,	..	..	23–24	17	..
	Maize oil,	..	..	18–20	14–16	..
	Cameline oil,	..	..	18–20	13–14	..
getable ing oils.	Linseed oil,	..	..	below 13–24	13·3–17·5	19·4 -20·6
	Hempseed oil,	..	..	17–19	14–16	16·6
	Nigerseed oil,	..	..	25–26·6	..	..
	Poppyseed oil,	..	..	19–22	15·4–17	16·2
	Sunflower oil,	..	..	17–24	17–18	..
	Walnut oil,	..	..	15–20	16	..
nimal ils and fats.	Neatsfoot oil,	..	..	29·8–30·8	..	26·5
	Tallow (beef),	42–44	45–47	45	..	38·3 -46·3
	,, (mutton),	49–50	53–54	46–49	..	41·5 –48·3
	Bone fat,	..	..	30	28	..
	Horse ,,	..	..	37·5–39·5	37·3–37·7	33·7
	Lard,	43–44	46–47	35–44	32·5–39	42·0
farine mal oils and id wax.	Sperm oil (inc. Arctic),	..	..	10·3–13·3	..	8·6 -11·9
	Whale oil,	..	..	14–18‡	..	23·9
	Seal oil,	..	..	22–33	..	15·0
	Cod liver oil,	..	..	..	..	13·9 -24·3
x (solid).	Wool fat,	..	..	52·6§	..	..

* 208 samples by De Negri and Fabris.

† All observers; the lower numbers obtained with Californian oils.

‡ 27° Jean.

§ Archbutt.

throughout, the mercury is watched closely. At first it will fall slowly, but at a certain point it will rise a few tenths of a degree, sometimes 2 or 3 degrees, and will then remain stationary for a short time before commencing to fall again. The point at which it remains stationary is the '*titre*' or solidifying-point of the fatty acids.

G.—REFRACTION TEST.

In the analysis of lubricating oils, the refractometer will be found a useful though not an indispensable instrument. The kind of instrument employed may be one such as Abbe's, by which the index of refraction of the oil is measured, or a differential refractometer, such as that of Trannin or Amagat and Jean, in which the deviation of the ray is measured on an arbitrary scale.

The following table contains the refractive indices for the D line of some oils as determined by Abbe, Strohmer, Holde and others with Abbe's refractometer:—

TABLE LIII.—REFRACTIVE INDICES.

Oils, in order of their Refractive Indices.	Index of Refraction	
	at 15° C.	at 20° C.
Neatsfoot oil, ...	1·467 –1·471	...
Olive oil, ...	1·4670–1·4717	1·4690
Sperm oil, ...	...	1·470
Rape oil, ...	1·4720–1·4757	1·472–1·475
Cotton seed oil, ...	1·4743–1·4752	1·4748
Sesamé oil, ...	1·4748–1·4762	...
Mustard oil, ...	1·4751–1·4760	...
Poppy oil, ...	1·478	...
Castor oil, ...	1·4795–1·4803	1·490
Walnut oil, ...	1·4804	1·491
Cod liver oil, ...	1·4800–1·4852	1·4800
Whale oil, ...	...	1·483
Linseed oil, ...	1·4835	1·4780
Beechnut oil, ...	...	1·5000
Mineral lubricating oil, ...	1·490 –1·500	...
Rosin oil, ...	1·530 –1·550	...

The instrument generally employed for commercial purposes is the **Oleo-refractometer** of Amagat and Jean, the essential parts of which are shewn in section in fig. 68 (p. 200). It consists of a collimator and a telescope having a common axis, between which is fixed a hollow prism for containing the oil. The hollow prism A is a metallic cell, having opposite glass windows CC fixed at an angle of 107°, and surrounded by a bath of sheep's foot oil ('huile type') contained in the vessel BB, which is furnished with opposite parallel windows DD¹. The temperature of the oils in the

TABLE LIV.—TESTS OF OILS WITH AMAGAT AND JEAN'S OLEO-REFRACTOMETER.

Class.	Name of Oil, etc.	Refractometer Degrees at 22° C.	Initial of Observer.
Vegetable on-drying oils.	Olive oil, . . .	±0 to +3·5	P. J. B. & L.
	Arachis (earthnut) oil,	+5 to +7	P.
	” ” ”	+3·5 to +6·5	J. B. & L.
	Castor oil, . . .	+39 to +42·5	P. D. & R.
	” . . .	+37 to +46	J. B. & L.
egetable mi-drying oils.	Rape oil, . . .	+15 to +20	P. & J.
	Ravison oil, . . .	+20 to +24	P.
	Cottonseed oil, . .	+17 to +23	P. & J.
	Sesamé oil, . . .	+13 to +18	P. & J.
	” . . .	+45	B. & L.
	Beech nut oil, . .	+16·5 and +18	J.
	Cameline oil, . .	+32	J.
Vegetable drying oils.	Linseed oil, . . .	+48 to +54	P. J. B. & L.
	Hempseed oil, . .	+32 to +37·5	P. & J.
	Nigerseed ” . .	+26 to +30	P.
	Poppyseed ” . .	+30 to +35	P.
	” ” . .	+23·5 to +29·5	J.
	Sunflower ” . .	+35	P.
	Walnut ” . .	+35 to +36	J.
nimal oils.	Lard oil, . . .	±0 to +1	P.
	” . . .	+5·5	J.
	Neatsfoot oil, . .	−1 to −4	P. & J.
	Tallow oil, . . .	−1 to −5	P.
	” . . .	−15	J.
Marine nimal oils.	Sperm oil, . . .	−12 to −17	J. C.
	” (Arctic), .	−13 to −16	C.
	Whale oil, . . .	+42 to +48	P.
	” ” . . .	+30·5	J.
	Seal ” . . .	+30 and +36	P.
	Shark liver oil, . .	+29 to +35	P.
	Cod liver ” . .	+40 to +46	P.
	” ” . .	+38 to +53	J.
scellaneous.	Rosin oil, . . .	+78	J.

cell, B, and in the prism are kept at a constant temperature of 22° C. by means of an outer water-bath not shewn in the figure. The light rays from an ordinary gas flame placed at the end of the collimator G traverse the oils, and are focussed by the lens E¹ of the telescope upon the photographed scale H, and viewed through the magnifier M. The collimator has, instead of a slit, a moveable shutter with a sharp vertical edge, which throws part of the field into shadow, and the edge of this shadow is focussed sharply upon the scale.

In using the instrument, the prism A is first of all filled with some of the standard (sheep's foot) oil, similar to that contained in the outer cell; there is then no refraction; and the edge of the shadow if not exactly on the zero of the scale is adjusted to it by moving the shutter. The standard oil having been drawn off through the tap R, and the prism rinsed with ether and dried, the oil to be tested is introduced, having been previously brought to exactly 22° C. in temperature. The deviation is then read off upon the scale.

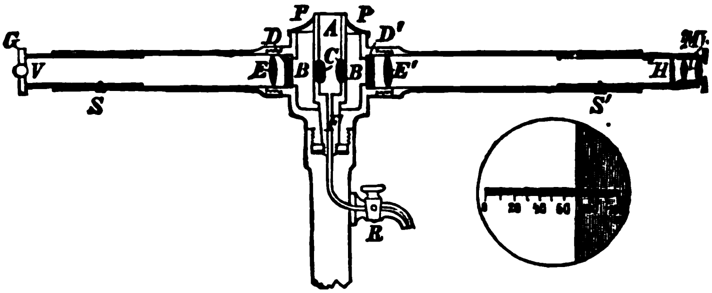

FIG. 68.

The results obtained by different instruments of this kind are only comparable if the angle of the prism of each instrument, the focal distance of the lens E¹, and the scale H are precisely the same. Allen states that this is not always the case, and that a sample of oil which shewed 4·5° in his instrument gave 6° and 11° respectively in two others. Therefore, every new instrument before being purchased should be tested with genuine samples of two or three typical oils, say olive, linseed, and castor, and the deviations compared with the numbers given in Table LIV. by Pearmain (P.) Jean (J.) Bruyn and Van Leent (B. and L.), and Chattaway (C.).

H.—COLOUR AND APPEARANCE.

The *colour* and *appearance* of lubricating oils are very variable. Some, like lard oil, are almost colourless, but most present a variety of shades of yellow, red, brown, and green. All the fixed oils and the refined mineral oils are transparent; the unrefined natural and reduced mineral oils are mostly opaque. Some exhibit fluorescence.

As the colour and appearance of oils depend upon the conditions under which they are viewed, this physical character, when of importance, must be estimated under definite conditions. Redwood uses for the purpose Lovibond's tintometer, observing the colour of the oil in a 2-inch cell.*

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* *Jour. Soc. Chem. Ind.*, ix. (1890), p. 14.

CHAPTER VII.

CHEMICAL PROPERTIES AND METHODS OF EXAMINATION OF LUBRICANTS.

A.—FREE ACID, OR ACIDITY.

I. Nature and Amount of the Free Acid in Oils.—Free acid in an oil or fat may consist of

(1) *Free fatty acid*, naturally existing in small quantity in most vegetable oils, or set free in larger quantity by the decomposition of a vegetable or animal oil during storage in a crude state, or by the action of sulphuric acid in the refining process;

(2) *Resin acids*, present as a natural constituent of rosin oil, or as added rosin;

(3) *Organic (petroleum) acids*, naturally existing in crude mineral oil;

(4) *Free sulphuric or other mineral acid* used in refining the oil and not properly washed out.

Free acid of any kind is objectionable in a lubricant for metallic surfaces, owing to its corrosive action. Free fatty acids have the additional disadvantage that the soaps formed by their action on metals dissolve in the oil and cause it to thicken and gum.

Mineral lubricating oils in the dark unrefined state contain small quantities of weak organic acids varying, according to Holde,* from 0·2 to 2·0 per cent. calculated as oleic acid; but the pale oils, when well refined, are almost perfectly neutral. Owing to their constitution, mineral oils are not capable, like animal and vegetable oils, of developing acidity by decomposition, though some of the contained hydrocarbons can undergo oxidation with formation of resinous and asphaltic products. Acidity of refined mineral oils is most likely to be due to the accidental presence of sulphuric acid, which is used in refining, but such an impurity is now rarely met with and would shew great carelessness in washing the oil.

All vegetable and animal oils, on the other hand, contain free fatty

* *Die Untersuchung der Schmiermittel*, p. 85.

acids in proportions varying from less than 0·5 per cent. to upwards of 50 per cent. The least acid oils are those refined with alkali, such as '*animal oil*' and *cottonseed oil;* the acidity of these oils varies, according to Archbutt's experience, from 0·08 to 0·26 per cent., *i.e.*, it is practically negligible. More acidity is met with in those oils which are refined with sulphuric acid, such as *rape oil*, which contains on an average about 3 per cent. of free (oleic) acid, varying, according to published figures,* from 0·52 to 6·64 per cent., but seldom exceeding 5 per cent. 230 samples of *refined rape oil* tested by Archbutt, all representing large contracts, gave the following results:—

Number of Samples.		Free (Oleic) Acid, per cent.
9	. . . . . .	1·1–1·9
60	. . . . . .	2·0–2·9
125	. . . . . .	3·0–3·9
33	. . . . . .	4·0–4·9
3	. . . . . .	5·0–5·7
230	(*Average*),	3·16 per cent.

Traces of free sulphuric acid are met with in rape oil which has been refined with this acid (see p. 301).

Those oils which are stored in a crude state, and are not afterwards chemically refined, often contain such large amounts of free fatty acids as to quite unfit them for use as lubricants.

Thus, in 9 samples of *palm oil*, Archbutt found from 11·9 to 78·9 per cent. of free (palmitic) acid.† Lewkowitsch states that he has found from 50 to 70 per cent. of free (palmitic) acid in a large number of commercial palm oils.

In 151 samples of *olive oil* from various sources, Archbutt found the following percentages of free (oleic) acid:‡—

TABLE LV.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
70	Spain, ...	25·1	1·5	5·5
36	Italy, ...	25·2	0·9	8·5
28	Sicily, ...	16·6	0·5	9·1
12	Candia, ...	16·8	5·5	9·5
3	Levant, ...	13·5	8·5	10·4
2	Zante, ...	8·7	4·8	6·7

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* Lewkowitsch, *Analysis of Oils, etc.*, p. 404.

† *Analyst*, ix. (1884), p. 171.

‡ *Jour. Soc. Chem. Ind.*, viii. (1889), p. 685.

Other observers have found from 1·0 to 27·2 per cent. of free (oleic) acid in olive oils.

In 25 samples of *tallow* examined by Deering * the following percentages of free (oleic) acid were found.

TABLE LVI.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
13	Russian, ...	12·20	2·20	5·48
4	Australian beef, . . .	8·85	1·75	4·47
4	„ mutton, . .	7·15	0·85	3·91
2	Town tallow, . . .	6·95	4·55	5·75
1	Unknown, . . .	2·10	...	...
1	Town tallow, 6 years old, .	25·0	...	...

Eighty-eight samples of *tallow* examined by Archbutt gave the following results:—

TABLE LVII.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
55	Home melted, . . .	11·90	1·40	4·89
9	Australian mutton, . .	12·84	1·00	4·84
11	South American beef, .	7·60	0·70	2·07
12	Unknown, ...	10·60	1·30	4·65
1	„	83·60	...	...

In 23 samples of *Indian castor oil*, examined by Deering and Redwood,† the acidity, calculated as oleic acid, ranged from 0·70 to 5·30 per cent., and averaged 2·58 per cent.; 6 samples of castor oil for lubricating, examined by Archbutt, contained from 1·47 to 2·70 per cent.; and Thomson and Ballantyne found, in two samples, 1·46 and 2·16 per cent., respectively. But Nordlinger found ‡ in 9 samples of expressed castor oil from 0·62 to 18·61 per cent. of free acid, or an average of 9·28 per cent.; whilst in 5 samples of extracted oil he found from 1·18 to 5·52 per cent., or an average of 2·78 per cent.

In 8 samples of *sperm oil*, seven examined by Deering and one by

* *Jour. Soc. Chem. Ind.*, iii. (1884), p. 540.

† *Ibid.*, xiii. (1894), p. 961.

‡ Lewkowitsch, *Analysis of Oils, etc.*, p. 8.

Thomson and Ballantyne, the acidity as oleic acid ranged from 0·55–2·64 per cent., and averaged 1·7 per cent.; in two samples of *Arctic sperm oil* it was 1·97 and 2·11 per cent. respectively, averaging 2·04 per cent. Fourteen samples of southern sperm oil, examined by Veitch Wilson,[*] contained from 0·5 to 2·0 per cent. of acidity, averaging 1·32 per cent.; and 29 samples of Arctic sperm oil contained from 0·5 to 3·0 per cent. of acidity, averaging 1·78 per cent. Therefore, Arctic sperm oil is a little but not much more acid than southern sperm.

Acidity is not the same as *rancidity*. Ballantyne [†] has shewn that oils can become rancid without the liberation of any free acid whatever, and the converse is also true. The researches of Ritsert and others have proved that the changes which produce rancidity of oils are due to oxidation.[‡]

The acidity of most fatty oils tends to increase by keeping, but it is a mistake to suppose that the change, as regards refined oils, is rapid enough to be of any practical importance. Thus Ballantyne[†] found that olive, rape, castor, and arachis (ground nut) oils remained unchanged in acidity for six months, whether kept in the dark in corked bottles or exposed freely to sunlight and air. It has been stated[§] that palm oil is exceptionally liable to increase in acidity by keeping; but some neutral palm oil prepared by Archbutt, after being kept in a stoppered bottle in a dark cupboard for 14 years was found to contain only 0·4 per cent. of acidity, calculated as palmitic acid, all of which may have been originally present, as the acidity was not determined after the oil had been purified.

II. **Effects of Free Fatty Acids in Lubricants.**—Burstyn,[||] who was one of the first to pay attention to the corrosive effects of fatty oils upon axles and bearings, shewed, in 1876, that the action of olive oil on brass was greater the more acid the oil. It is, therefore, surprising that Redwood[¶] and others who have been at much pains in investigating the relative action of various fatty oils upon metals did not determine the amount of free acid contained in the oils they experimented with. This omission makes their experiments almost valueless, as the different effects observed may have been entirely due to differences in the acidity of the different oils, and not to any difference in the properties of the oils themselves.

Not only is it probable that neutral fatty oils have no chemical action on metals, but it is doubtful whether even the free fatty acids can exert much action in the absence of air and moisture. Thus Fox[**] suspended thin strips of lead in the mixed fatty acids prepared from olive and linseed oils and found that after having been heated for several days to 220° F. the lead had not lost weight. E. Donath* took bright, accurately weighed strips of iron, copper, brass, and zinc, and completely immersed some in strongly acid olive oil and others in crude oleic acid. At the end of three weeks, the strips were found to have suffered very little loss of brightness and a scarcely perceptible loss of weight. Even when the oils were kept heated to 70°–80° C. (158°–176° F.) for several days, the metals were not attacked. But if, previous to immersing the metals in the acid oils, the latter were thoroughly emulsified with air, or especially with water, by vigorous shaking, corrosion readily took place. Donath concluded from these experiments that the corrosive action on metals of lubricating oils containing free fatty acids depends to a great extent upon whether the oiled surfaces come into contact with atmospheric oxygen, and whether, by condensation or other means, water gets into the oil. It is difficult to account in any other way for the very erratic manner in which corrosion sometimes takes place, such as is illustrated by the following experiment made by Archbutt several years ago.

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[*] Carpenter and Leask, *Soap, Candles, Lubricants, and Glycerin*, p. 298.

[†] *Jour. Soc. Chem. Ind.*, x. (1891), p. 29.

[‡] See Lewkowitsch, *Analysis of Oils, etc.*, p. 10; also Mjoën, *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 253.

[§] Groger, *Jour. Soc. Chem. Ind.*, viii. (1897), p. 202.

[||] *Dingler's Polyt. Journal*, ccxvii., p. 314.

[¶] I. J. Redwood, *Jour. Soc. Chem. Ind.*, v. (1886), p. 362.

[**] *Analyst*, viii. (1883), p. 116.

Four samples of *railway wagon grease*, each composed, in the same proportions, of tallow, palm oil, soap, and water, but containing respectively 0·4, 1·4, 1·6, and 4·0 per cent. of free fatty acid, were taken, also a sample of very acid palm oil, free from water, containing 72·2 per cent. of free (palmitic) acid. Into each of these five specimens of grease, etc., two strips of bright steel were inserted, and after an interval of four months they were taken out, cleaned and examined, with the following results:—

Strips immersed in	Free Fatty Acid per cent.	Condition of the Steel after 4 Months' immersion.
Grease No. 1, .	0·4	Both strips bright.
Grease No. 2, .	1·4	" "
Grease No. 3, .	1·6	1 strip bright, 1 deeply corroded in one spot.
Grease No. 4, .	4·0	Both strips deeply corroded on one side.
Acid palm oil, .	72·2	Both strips merely stained and not corroded.

If fatty acids alone can attack steel, the two strips immersed in the very acid palm oil should have been the most corroded, instead of which they were merely stained, whilst the strips immersed in the grease containing only 4 per cent. of free fatty acid were both deeply corroded, doubtless because of the simultaneous presence of water. It will be observed that the most acid grease proved to be the most corrosive of the four.

Oleic acid, water, and iron filings, if heated together in a test-tube, react briskly, hydrogen being evolved and brown oleate of iron formed. This compound is decomposed, by oxidation, into iron peroxide and free oleic acid, which again attacks more iron; in this way a comparatively small quantity of the free fatty acid has been known to perforate wrought iron plate more than ½ inch in thickness.*

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* *Dingler's Polyt Journal*, ccxcix., p. 186; *Jour. Soc. Chem. Ind.*, xiv. (1885), p. 283.

Although a metal in stationary contact with a cold solid grease containing free fatty acid may undergo serious *local* pitting, as proved by the above experiments, the corrosive action upon a brass or journal of the free fatty acid existing in a fluid oil, or in a grease lubricating a journal in motion, may escape notice, because it is spread over the whole of the rubbing surfaces. But the effect will be observable in the thickening of the oil and in the formation of gummy deposits. Allen has already recorded the following instance of this, which was communicated to him in 1883. A mixture of olive oil with from 10 to 15 per cent. of mineral oil, which had been taken out of a railway carriage axle-box much thickened after about three weeks' use, was found to be of a deep green colour and to contain in solution much copper and zinc. Some of the oil was dissolved in ether and shaken with dilute nitric acid to extract the dissolved metals; the ether was then evaporated, and the oil was recovered with its original colour and almost its original fluidity restored. From this it is evident that the thickening and gumming of fatty oils on bearings, generally attributed solely to oxidation, may be due partly to soaps formed by the chemical action of the free fatty acids upon the metal of the bearing, dissolving in and thickening the oil.

III.—**Determination of Acidity.**—The acidity of lubricating oil, which, as already stated, may be due to the presence of more than one description of free fatty or resin acid, or (rarely) to a mineral acid, is generally determined volumetrically and expressed either as oleic acid or as sulphuric acid or sulphuric anhydride. In this country it is usual to express the acidity of a fixed oil or fat in terms of oleic acid, on the Continent the acidity is frequently stated as sulphuric anhydride. Another method of expression, adopted by Benedikt, is known as the '*acid value*,' which is the *number of milligrammes of potash* (KOH) *required to neutralize the free acid in 1 grm. of oil.* Koettstorfer has proposed to express the acidity in '*degrees*,' which are the *number of c.c. of normal alkali required to neutralize the acidity of 100 grms. of oil.* Koettstorfer's degrees have the advantage to a chemist that they are at once converted into any required acid, if multiplied by the saponification equivalent of that acid ÷ 1000. The relation of the different methods of expression is shewn in the table, on the following page, by Benedikt.

For the estimation of total acidity, 5–10 grms. of the oil may be completely dissolved in a neutralized mixture of ether (4 pts.) and absolute alcohol (1 pt.) and titrated with an alcoholic decinormal solution of caustic soda, using phenolphthalein as indicator; or, the oil may be merely shaken up in a flask with neutralized methylated spirit

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* V. Wartha, *Dingler's Polyt. Journal*, ccxv., p. 115; Stock, *Chem. News*, xxxix. (1879), p. 6.

Degrees; = c.c. of normal alkali required to neutralize 100 grms. of oil.	Acid Values; = milligrms. of KOH required to neutralize 1 grm. of oil.	Oleic Acid, per cent.	Sulphuric Anhydride, per cent.
1	0·561	0·282	0·040
1·782	1	0·5027	0·0713
3·546	1·9863	1	0·1418
25·000	14·025	7·05	1

(which dissolves the free acid, leaving most of the neutral oil insoluble) and titrated with aqueous caustic soda solution. The latter method is simpler, and is sufficiently accurate; it is therefore preferable for technical purposes. The solutions required are:—

Normal (aqueous) caustic soda solution. 1 c.c. = 0·282 grm. Oleic Acid.

Phenolphthalein solution. An alcoholic solution, containing 3 grms. phenolphthalein in 100 c.c., neutralized by shaking with dry precipitated calcium carbonate and filtering.

Neutralized methylated spirit; prepared by filling a stoppered bottle of about 500 c.c. capacity with ordinary methylated spirit, adding 10 c.c. of phenolphthalein solution, and dropping in normal caustic soda solution from a burette until the liquid assumes a faint permanent pink colour.

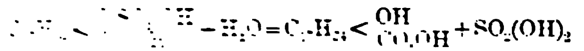
To determine the acidity of a fluid oil in terms of oleic acid, weigh 28·2 grms. of the oil into an Erlenmeyer flask of about 250 c.c. capacity, add 50 c.c. of neutralized alcohol and 2 c.c. of phenolphthalein solution. Then add normal caustic soda solution from a burette, cautiously at first, but afterwards in quantities of 0·5 to 1·0 c.c. or more at a time if the crimson colour at first formed disappears quickly on shaking. When the colour begins to disappear slowly, cork the flask and shake it violently, then add the soda in smaller quantities, finally drop by drop, vigorously shaking the corked flask after the addition of each drop, until the alcoholic liquid is permanently coloured a faint pink. The number of c.c. of normal caustic soda solution used is the percentage of free acid, expressed as oleic acid, in the sample. If the quantity of oil available is small, 2·82 grms. may be titrated with *decinormal* soda, which will give the same result.

A solid fat, such as tallow, may be titrated in the same way as a fluid oil, if the contents of the flask be kept sufficiently heated to maintain the fat in a melted condition. In weighing out the fat, some of it is first melted in a beaker and poured while melted into the counterpoised flask until the weight is nearly made up. The flask is then removed from the balance and allowed to become quite cold. It is then replaced, and the exact weight is made up by adding a little more fat. In titrating palm oil, which is sometimes deep red in colour, the half or quarter of 28·2 grms. may be taken and mixed with 100 c.c. of alcohol instead of 50 c.c.; the colour change can then be sharply detected even with very red samples. The volume in c.c. is multiplied by 2 or 4 as the case may be, to get the percentage of acid.

Very dark coloured oils, in which the colour change cannot be detected by the above method, should be very well shaken with two or three times their volume of neutralized alcohol, then poured into a separating funnel and left for the liquids to separate. The oil is drawn off into the [illegible] and shaken again with an equal volume of alcohol, whilst the [illegible] the separator is drawn off into a clean flask. The [illegible] is again returned into the funnel and allowed to [illegible] shaken a third time with alcohol. [illegible] extracts having been mixed with the first, [illegible] and the liquid is titrated with caustic soda.

[illegible] must be tested for separately, as the above methods [illegible] between fatty and mineral acid. To detect the presence [illegible] a known quantity, say 25 c.c., or about the same [illegible] and well shake it in a separating funnel with [illegible] the water has quite separated from the oil [illegible] water into a flask, and add to the *cold* liquid [illegible] indicator, which is unaffected by fatty acids, [illegible] mineral acid will tinge the liquid red. If free [illegible] may be again shaken several times with [illegible] water, until all the acid has been washed out, and [illegible] may then be neutralized by adding normal caustic [illegible] just changes to yellow. 1 c.c. of normal [illegible] grm. of sulphuric acid, or 0·040 grm. of [illegible] quantity of oil taken. The neutralized solution [illegible] small volume and portions tested with appropriate [illegible] the nature of the acid present. (See also [illegible]

[illegible] fatty acids must be well boiled with water [illegible] the mixture, in order to decompose the compound [illegible]—



$$[illegible] - H_2O = C_{17}H_{34} < \begin{matrix} OH \\ CO.OH \end{matrix} + SO_2(OH)_2$$

[illegible] hydroxy-stearic acid. sulphuric acid.

[illegible] the aqueous liquid, after separation from [illegible] evaporated down to about 70 c.c., filtered bright [illegible] standard soda solution, using methyl orange as [illegible] afterwards be acidified, precipitated with barium [illegible] weighed, if desired.

[illegible] **estimation of free fatty and resin acids.**—The free fatty [illegible] that may be separated and weighed in the [illegible]

[illegible] dissolved in ether and rinsed into a separating [illegible] water have been placed to seal the tap. [illegible] repeatedly with small quantities (10–20 c.c. [illegible] containing 20 c.c. of a 10 [illegible] alcohol made up with water to [illegible] 10 c.c. of the dilute soda solution, [illegible] 1·4 grm. oleic acid). The mixed [illegible] with a little ether to remove traces of oil, [illegible] and shaken with ether to dis- [illegible]. After washing the ethereal solution [illegible] the residue is heated on the water-oven [illegible] be separated and estimated by [illegible] neutral oil may be recovered [illegible] solution.

[illegible] **Amount of Free Acid permissible in Lubricants.**—The [illegible] free acid permissible in a lubricating oil depends upon the nature of the oil and the purpose it is used for. A refined (pale) mineral oil should not contain any acid whatever; but the dark-coloured 'reduced' oils may be expected to contain traces of weak organic acids varying, according to Holde, from 0·2 to about 2·0 per cent., calculated as oleic acid. Free mineral acid, which can only occur through imperfect refining, should not be permitted in any oil; but some free fatty acid must be allowed in fixed oils and fats. Experience shews that 4 per cent. of free fatty acid, calculated as oleic acid, is a practicable working limit, and no olive oil, tallow, or other oil containing more than this proportion of acidity should be used for lubricating. The less there is below this amount the better the oil.

V. **Process for refining small quantities of oil.**—Neutral oil or tallow required in small quantity for delicate mechanism, instruments, brass taps, etc., can be prepared as follows:—Take a good commercial sample of the oil or fat, containing not more than say 5–7 per cent. of free (oleic) acid, and place it in a bottle with one-third of its volume of caustic soda solution prepared by mixing a 5 per cent. aqueous solution of caustic soda with half its volume of methylated spirit. Add also some phenolphthalein. Stand the bottle in hot water, so as to raise the temperature of the contents to about 150° F., and then shake the oil and soda together, thoroughly, but not too vigorously. If the crimson colour of the phenolphthalein is bleached, add more soda until the colour remains permanent on continued shaking. Then allow the liquids to separate, while hot, in the bottle or in a separating funnel, and siphon or tap off the lower liquid. Wash the oil by shaking it a few times with a mixture of water 2 volumes and methylated spirit 1 volume, allow to stand until the water has separated, filter the oil through a dry filter, and heat it in the water-oven to a temperature not exceeding 212° F. until bright.

B.—DETECTION OF SAPONIFIABLE AND UNSAPONIFIABLE OIL.

Pure mineral oils and refined rosin oil free from resin acids are chemically indifferent towards alkalis, but all the fixed oils, fats, and waxes when heated with caustic soda or potash are saponified, with formation of glycerol or wax alcohols and soaps. This difference of behaviour is the basis of the processes for the detection and estimation of fixed (saponifiable) oils and hydrocarbon (unsaponifiable) oils in the presence of each other.

I. Detection of Fatty Oil in Mineral Oil.

Lux's test, improved by Ruhemann,* depends upon the property possessed by quite small quantities of soap of causing the gelatinization of mineral oil, as well as upon the frothing or foaming of soapy liquids when heated.

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* *Jour. Soc. Chem. Ind.*, xii. (1893), p. 470.

[illegible] mineral oil are placed in a dry test tube with a [illegible] the tube is heated in a paraffin bath for 15 [illegible] in the case of pale coloured oils, or 250° [illegible] cylinder oils. If very small quantities [illegible] are to be looked for, a duplicate test is [illegible] metallic sodium instead of caustic soda. On [illegible] and allowing them to cool, the presence of [illegible] the gelatinization (complete or partial) of [illegible] the appearance, on the surface of the [illegible] which is proportional to the quantity [illegible] present. Both gelatinization and the soapy froth may [illegible] Holde states* as the result of a large number of experi[illegible] this test as little as [illegible] per cent. of fatty oil may be detected [illegible] 2 per cent. in dark-coloured oils, and 1 per cent. in [illegible]

II. Detection of Mineral Oil in Fatty Oil.

The following test by Holde† depends upon the fact that an [illegible] solution of pure soap remains clear on the addition of a [illegible] quantity of water; but in the presence of mineral oil, the addition of water causes the formation of a turbidity, due to the precipitation of the unsaponified mineral oil.

[illegible] about the size of a pea, is heated in a test tube [illegible] until dissolved; 3 or 4 drops of the [illegible] the liquid is boiled for 1 minute. Or, [illegible] solution of potash in alcohol (see [illegible] drops of oil. To the soap [illegible] water is gradually added, well mixing after [illegible] have been added altogether. If un[illegible] solution remains clear, even when mixed with [illegible] water; but the presence of even 1 per cent. [illegible] the formation of a turbidity. Careful observation [illegible] turbidity produced by a very small [illegible] 2 per cent. sometimes disappears again on [illegible] and may therefore easily be overlooked. Rosin [illegible] 12 per cent., is not detected. The [illegible] the fluid waxes do not precipitate at [illegible] dissolved in the soap solution for some [illegible] therefore, this test can be used for the detection of [illegible] (Bailey & Burgess‡).

C.—THE SAPONIFICATION VALUE.

I. Meaning and Use of this Value.

The reactions between caustic alkalis and the compound ethers contained in oils and fats take place in definite proportions, and in the case of any single ester can be represented by an equation (see

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* *Die Untersuchung der Schmiermittel*, p. 111.

† *Ibid.*, p. 114.

‡ *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 426.

p. 100). Thus, one molecule of every glyceride requires for saponification three molecules of potash, whilst one molecule of the ester of a monohydric alcohol requires one molecule of potash. The quantity of potash required for the saponification of any single ester, such as pure stearin or olein, can therefore be calculated, and serves to identify it, but the quantity required to saponify the mixed esters known as fixed oils, fats, and waxes can only be ascertained by experiment, and when expressed as a percentage[*] is called the '*saponification value*' of the oil, fat, or wax.

Reference to the table on p. 213 will shew that the majority of saponifiable oils require about the same percentage of potash for saponification, the exceptions being rape oil, mustard oil, castor oil, and some of the fish oils, which require less than the average, and butter fat, palm nut oil, coconut oil, and porpoise and dolphin jaw oils, which require considerably more. The waxes have characteristically low saponification values. Hydrocarbon oils, of course, have none. Hence a knowledge of the saponification value enables us to detect, and frequently to approximately estimate the proportion of hydrocarbon oil in a mixture; to identify in a pure state those oils and waxes which have characteristic values; and, to a limited extent, to detect the adulteration of one fatty oil with another having a different saponification value.

II. Determination of the Saponification Value.

For the determination of this value, the following reagents are required:—

Approximately seminormal alcoholic potash, made by dissolving about 18 grms. of the purest obtainable potash in 500 c.c. of pure rectified alcohol. As potash 'pure by alcohol' usually contains about 20 per cent. of water, this solution will be about seminormal in strength; if anhydrous potash were used 14 grms. would be enough.

If made with impure spirit, the solution will rapidly assume a red or brown colour and will then be unfit for use, but if made with pure rectified alcohol it will slowly acquire a pale yellow tint which in no way interferes with the test. No difficulty will be experienced in dissolving the potash in the strong alcohol if the following plan be adopted:—Introduce the potash and the alcohol into a 500 c.c. test mixer, insert the stopper, and invert the cylinder so as to bring the potash to the upper end. Then lay the cylinder upon the bench and raise the upper end upon a block at such an angle that the potash will not slide to the bottom; it will then very rapidly dissolve. When solution is complete, well mix the contents of the cylinder, allow to stand over night, and filter through a dry filter paper into the reagent bottle, which should be closed by a rubber stopper and kept in a cool, dark cupboard.

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[*] Koettstorfer, who originated this test as a means for detecting the adulteration of butter, expressed his results in milligrammes of potash per gramme of fat, *i.e.*, in parts per 1000, and, with the exception of Allen (*Coml. Org. Anal.*), most authors have followed his example. The acetyl values of oils are similarly expressed, but the Hehner and iodine values have always been expressed in percentages. For the sake of uniformity the percentage system is adopted for all values given in this volume.

Seminormal hydrochloric acid, accurately standardized with pure sodium carbonate, which has been heated to just below redness for 5 minutes and cooled in a covered platinum crucible in a desiccator immediately before weighing. 1 c.c. of strictly seminormal acid neutralizes 0·02807 grm. KOH.

Phenolphthalein solution. (See p. 207.)

(*a*) **In determining the saponification value of a fixed oil or fat,** exactly 2·5 grms. are weighed into a small wide-necked flask* and 25 c.c. of the seminormal potash solution are added from a pipette.† Exactly the same volume of potash is then delivered into an empty flask of the same size and shape. The two flasks are closed by corks having a groove filed in the side for the escape of vapour. The 'blank' quantity is placed at once inside the water-oven. The flask containing the oil is first of all heated on a steam-bath until the alcohol commences to boil, it is then agitated with a rotary motion to and fro, so as to break up the oil into small globules and facilitate the saponification, care being taken not to splash the liquid up on to the cork. When (in the case of a pure fatty oil) the globules of oil have entirely disappeared, or when (in the case of a mixed fatty and mineral oil) the oil and alkaline solution have been thoroughly boiled and agitated together, the flask is placed inside the water oven. After fifteen minutes have elapsed, the 'blank' quantity is taken out, mixed with about 1 c.c. of phenolphthalein solution, and carefully titrated with the seminormal acid until the crimson colour is just bleached; the flask containing the saponified oil is then similarly treated, and from the relative volumes of acid used the saponification value is calculated as shewn by the following example :—

Weight of oil taken ; 2·5 grms.

Volume of $\frac{N}{2}$ acid used for the 'blank,' . . . 26·05 c.c.

" " " sample, . . . 10·55 c.c.

Difference ; = $\frac{N}{2}$ KOH required for saponification, 15·50 c.c.

Therefore, 100 grms. of oil required $15·5 \times 0·02807 \times 40 = 17·40$ grms. KOH for complete saponification ; *i.e.*, the saponification value is 17·40 per cent.

The quantity of potash used in this test should be largely in excess of the quantity required for saponification, and if it should be found on titrating with acid that the potash added has been nearly all used up, the test must be repeated, either with less of the oil or with a stronger potash solution. In general, correct results will be obtained by adhering to the proportions given above.

(*b*) *In testing mixed fatty and mineral oils*, especially when the proportion of mineral oil is large, it is safer to attach the flask, by means of a good ordinary cork, to a reflux condenser, and boil for an hour or more to ensure

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* The balance case should have a side door, by opening which the oil can be dropped from the bottle straight into the flask ; the weighing of an exact quantity is then quite easy.

† The pipette used to deliver the potash solution should have a rather wide jet, and should be held vertically in the centre of the neck of the flask until the liquid has run clean out ; it should then be immediately removed, and not allowed to drip or drain.

LVIII.—Saponification Values of Oils, Fats, and Waxes.

ass.	Name of Oil, etc.	*Saponification Value.* KOH required to saponify 100 parts of the substance.
ble non-oils and ts.	Olive oil,	18·5 -19·6 ; usually about 19·0 *
	Olive kernel oil,	18·23-18·38
	Arachis (earthnut) oil,	18·8 -19·7
	Castor oil,	17·6 -18·7
	Palm oil,	19·6 -20·2
	Palm nut oil,	24·8 -25·0
	Coconut oil,	24·6 -26·8
	Japan wax,	21·4 -22·2
	Cottonseed stearin,	19·5
le semi- g oils.	Rape oil,	17·0 -17·5 (17·6 ?)
	Ravison oil,	17·8 -17·9
	Mustard oil (black),	17·4 -17·5
	Mustard oil (white),	17·0 -17·4
	Cottonseed oil,	19·1 -19·7
	Curcas oil,	19·2 -19·3
	Sesamé oil,	18·8 -19·5
	Beech nut oil,	19·1 -19·6
	Brazil nut oil,	19·3
	Maize oil,	18·8 -19·3
	Cameline oil,	18·8
le drying ils.	Linseed oil,	18·8 -19·5
	Hempseed oil,	19·0 -19·3
	Nigerseed oil,	18·9 -19·2
	Poppyseed oil,	19·0 -19·8
	Sunflower oil,	18·8 -19·4
	Walnut oil,	18·9 -19·7
l oils and ats.	Lard oil,	19·1 -19·6
	Neatsfoot oil,	19·4 -19·7
	Tallow (beef, mutton, and home refined),	19·0 -19·8
	Bone fat,	19·1
	Horse fat,	19·5 -19·7
	Lard,	19·5 -19·7
e animal nd fluid xes.	Sperm and bottlenose oils,	12·3 -14·7
	Porpoise body oil,	21·6 -21·9
	Porpoise jaw oil, strained from solid fat,	25·3 -27·2
	Porpoise jaw oil, unstrained,	14·4
	Dolphin body oil,	19·7
	Dolphin jaw oil, strained from solid fat,	29·0
	Whale oil,	18·8 -19·4
	Seal oil,	18·9 -19·6
	Menhaden oil,	18·9 -19·2
	Sardine oil (Japanese),	19·0 -19·2
	Shark liver oil,	14·0 -19·8
	Cod liver oil,	17·1 -19·3
(solid).	Wool fat,	8·2 -13·0
	Spermaceti,	12·5 -13·6
	Beeswax,	8·8 -10·7
	Carnauba wax,	7·8 - 9·5
n oils.	Blown rape oil,	19·5 -20·3
	Blown ravison oil,	20·0
	Blown cotton seed oil,	21·3 -21·6
	Blown seal oil,	22·1
carbons.	Mineral oil,	nil.
	Vaseline,	
	Paraffin wax and cerasin,	

* De Negri and Fabris, 203 samples.

complete saponification, the 'blank' quantity of potash solution being boiled in the same way and for the same length of time. In testing two or more oils at the same time, if there are not enough condensers, the potash solution should be measured into all the flasks, and those which have to wait kept closed with rubber stoppers until condensers are available, each liquid being titrated with acid as soon as it has been removed from the condenser. Wool oil [illegible] cannot be completely saponified in this way, and must be heated in a closed [illegible] under pressure with double normal alcoholic potash for about [illegible].

The terms 'saponification value,' 'Koettstorfer value,' '*alkali value*,' employed by various authors, have the same meaning. The term 'saponification equivalent,' used by Allen,* means the weight of oil in grams saponified by 56·1 grams of potash, or by one equivalent of any other alkali. Thus the

saponification value % : 100 :: 56·1 : the saponification equivalent

$$\text{the saponification equivalent} = \frac{5610}{\text{the saponification value}}.$$

The saponification equivalent of any glyceride is one-third of the molecular weight; in the case of the ester of a monohydric alcohol it is identical with the molecular weight, and the same is true of the free fatty acids.

[illegible].—APPROXIMATE ANALYSIS OF MIXED LUBRICATING OILS.

It is obvious that the composition of a mixture of mineral oil and a single known fatty oil can be calculated from the saponification value of the mixture. Thus if a mixture known to consist of rape oil and mineral oil have a saponification value, per cent., of 8·2, the percentage of rape oil in the mixture must be nearly 8·2 × 100 ÷ 17·3 = 47·4, and the percentage of mineral oil 100 − 47·4 = 52·6.

When the nature, and therefore the saponification value, of the fatty constituent is unknown, the possible error of the method becomes greater, but Thomson† has shewn by the analysis of several mixed lubricating oils that the results obtained are sufficiently correct for commercial purposes when rapidity is of supreme importance. He adopts 19·65 per cent. as the mean saponification value of the fatty constituent, and considering the extent to which blown rape oil is used in the preparation of commercial lubricating oils, this figure would be likely to give good results in perhaps the majority of cases. Very nearly the same result would be obtained by taking the whole number 20. Then, the saponification value, per cent., of the mixture × 5 is the approximate percentage of saponifiable oil, and the percentage of mineral oil is obtained by subtracting this number from 100.

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* *Comm. Org. Anal.*, vol. ii. pt. i. p. 53.

† *Chem. News*, lxv. (1892), p. 27.

After determining the saponification value, Gripper again raises the alcoholic liquid to the boiling-point and pours it on to a filter paper which has been saturated with boiling water. The alcoholic solution of soap, etc., quickly runs through, leaving the greater part of the hydrocarbon oil on the filter. After washing once with boiling water, thé specific gravity of this oil is determined by the alcohol method (p. 170).

E.—ESTIMATION OF TOTAL UNSAPONIFIABLE MATTER.

If the solution obtained by saponifying a mixed fatty and mineral oil with potash or soda be shaken with an immiscible solvent, such as ether or petroleum ether, or if the dried soap be extracted with petroleum ether or chloroform, all the unsaponifiable hydrocarbon oil is dissolved out, and may be obtained in a separate state by evaporation of the solvent, and the amount estimated by weighing.

Commercial fixed oils and fats, quite free from added hydrocarbons, contain small quantities of unsaponifiable substances which, under similar circumstances, are extracted by the solvent; but in most cases the natural unsaponifiable matters (chiefly phytosterol, cholesterol, etc.) do not amount to more than from 1 to 1·5 per cent. The waxes, however, such as sperm oil, wool fat, beeswax, and carnauba wax, yield on saponification, instead of glycerol, monohydric alcohols which dissolve in the ether and may amount to from 35 to 55 per cent. of the wax saponified. Shark liver oil also frequently yields on saponification considerable quantities of solid alcohols.

In the analysis of lubricants, therefore, the determination of the unsaponifiable matter is not only a means of separating and estimating the proportion of hydrocarbon oil present, but it is also a means of identifying sperm oil and the waxes, ascertaining their purity, and estimating their proportion in mixtures.

I. General method for the determination of unsaponifiable matter in an easily saponifiable oil, fat, or fluid wax, such as rape oil, sperm oil, etc.

The following reagents are required :—

50 *per cent. Caustic Soda Solution.*—250 grms. of pure caustic soda, from sodium, are dissolved in cold water in a deep porcelain basin, and the solution, when cold, is made up to 500 c.c. If not clear, it may be filtered through ordinary filter paper. The solution is preserved for use in a bottle closed by a rubber stopper. 2 c.c. contain, approximately, 1 grm. NaOH.

Alcohol.—Methylated alcohol free from naphtha may be used, but pure rectified alcohol of 0·830 sp. gr. is preferable.

Ether.—Redistilled methylated ether of sp. gr. 0·725.

(*a*) **The Process.**—Pour about 10 c.c. of the oil into a very small lipped beaker and take the exact weight. Then take a deep porcelain basin, [illegible] of the beaker [illegible] a little too [illegible] the end of the [illegible] a little boiling [illegible]

[illegible] a small [illegible] have [illegible] a thick glass and [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

(c) [illegible] will present the appearance of a [illegible] Probably [illegible] present; [illegible] of small quantities of water, as in (b), will cause [illegible]

(d) The liquids form an *opaque viscid emulsion*. In this case there is probably not enough alcohol, and the remedy is to add more alcohol, 2 or 3 c.c. at a time, and cautiously mix until separation into two layers occurs either at once or on standing for a few minutes.

When the liquids have properly separated (allow about 10 minutes for *complete separation to occur*), draw off the layer of soap solution into another separator.† Shake this again with ether (using about 70 c.c. this time), run it off into a third separator, and shake a third time with ether. Then mix all three ethereal layers in one separator, wash twice, each time with 10 c.c. of a 1 per cent. caustic soda solution containing 10 per cent. of alcohol, then wash six times with pure water, using 10 c.c. each time. Thoroughly drain off the water, pour the ethereal solution (in two portions) into a light, wide-necked, 8-oz. flask, previously weighed, and distil off the greater part of the ether from a hot water-bath. Then place the flask on the top of the water oven, and let it stand there until the ether and water have entirely evaporated. The evaporation of the water may be hastened by surrounding the flask with a beaker from which the bottom has been removed, and by frequently running the liquid round the sides of the flask. Then let the flask cool, and weigh it. Replace it on the oven for 10 or 20 minutes, cool, and re-weigh. Repeat this until practically constant. By subtracting the tare of the empty flask, the weight of unsaponifiable matter in the 5 grammes of oil taken is obtained.

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* Made by cutting all but about 1½ inches of the stem off a bulb funnel, and filing the end obliquely.

† Before removing the stopper, drop a little ether upon the outside of the separator and blow upon it, so as to cool the glass by evaporation; this will reduce the pressure of the ether vapour inside, and will prevent drops of liquid from being expelled when the stopper is removed.

If the above directions are carried out, the whole operation, from weighing out the oil to the final weighing of the unsaponifiable matter, can be completed within 3 hours. Ordinary ether is, in the writer's experience, preferable to petroleum ether, which is recommended by some chemists for extracting the unsaponifiable matter; it boils at a lower and a constant temperature, evaporates more readily, and leaves no residue; whereas petroleum ether, as purchased, cannot be depended upon to evaporate without residue, and must, as Lewkowitsch points out,[*] always be re-fractionated, involving considerable trouble. When ordinary ether is used, it may be completely evaporated at such a low temperature that light mineral oil, which is sometimes used for adulterating rape and other oils, can be detected and estimated without appreciable loss. Lewkowitsch states[†] that ordinary ether extracts larger quantities of soap than petroleum ether; but, for ordinary purposes, the amount of soap extracted when the process is conducted as described above is quite negligible.[‡] In cases where great accuracy is required, traces of soap and saponifiable matter contained in the product of the first extraction may be removed by boiling it with alcoholic soda and re-extracting with ether.

(*b*) *Modification in presence of much Mineral Oil.*—When much mineral oil is present, saponification in a basin is not a satisfactory method, because the oil does not entirely dissolve, but visible drops of, chiefly mineral, oil remain suspended in the liquid, and a more vigorous and longer boiling is desirable in order to insure complete saponification. In such cases, it is better to weigh the oil into a flask and boil it with the alcoholic soda solution under a reflux condenser for an hour or more. Then pour the contents of the flask into a basin, boil down gently to 10–15 c.c., and proceed exactly as directed above, rinsing the flask as well as the basin into the separator with, first, a little hot water, and then with ether from the wash bottle.

(*c*) *Modification in presence of Wool Fat.*—Wool fat and lubricants containing it must be heated with alcoholic soda solution of double normal strength in a closed bottle under pressure for about two hours to insure complete saponification.[*] An ordinary 4-oz. reagent bottle of fairly thick glass answers very well for this purpose, and after the oil or fat and the alkaline solution have been introduced[†] an indiarubber stopper[‡] is inserted and tied firmly down with string, leaving a loop at the top. This loop is suspended from a glass rod or stout brass wire fixed horizontally in a clamp over a can of warm water, so that the bottle is immersed up to the neck in the water, which is then raised to boiling-point and kept gently boiling, being replaced from time to time as it evaporates. If the bottle will not sink sufficiently, a strip of lead may be wrapped round it and fastened by an indiarubber band. The bottle is removed from the water occasionally and the contents well mixed by circular agitation, taking care not to splash any liquid on to the rubber stopper. When saponification is complete the bottle is allowed to cool, the stopper is then taken out, the liquid is poured into a basin and proceeded with as directed above.

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[*] *Analysis of Oils, etc.*, p. 219.

[†] *Ibid.*, p. 218.

[‡] In a subsequent paper (*Jour. Soc. Chem. Ind.*, xv. (1896), p. 13) Lewkowitsch admits that it is safest to employ ordinary ether for extraction, but he advises incinerating the unsaponifiable matter and calculating the soap present, if any, from the alkalinity of the residue. He describes an experiment in which a sample of shark liver oil gave 10 per cent. of unsaponifiable matter, consisting of wax alcohols from spermaceti, when ordinary ether was employed, whereas petroleum ether only extracted from 1·38 to 3·73 per cent.

The formation of a *layer of white insoluble flocks* between the aqueous and ethereal liquids is characteristic of wool fat, and often indicates its presence. Lewkowitsch has shewn that these flocks consist of an insoluble soap formed from fatty acids of high molecular weight; they do not belong, therefore, to the unsaponifiable matter, and should be separated from the washed ethereal liquid by filtration through a small dry filter paper. The same device is often useful for removing drops of water which might otherwise find their way into the distilling flask.

(*d*) *Modification in presence of Beeswax.*—Owing to the sparing solubility of myricyl alcohol in most cold solvents, the above method cannot be applied to the analysis of beeswax, carnauba wax, and substances containing large quantities of myricyl alcohol.[§] When beeswax and carnauba wax are boiled with alcoholic soda solution under a reflux condenser, saponification readily takes place, and a clear or almost clear solution is obtained in a short time, but immediately the liquid begins to cool not only the wax-alcohol but the soap (sodium cerotate) solidifies on the sides of the flask, and before the contents have become nearly cold they form an almost solid mass. The best way to proceed in such cases (which are unlikely to occur in connection with the analysis of lubricants) is to extract the *dry* soap with chloroform as recommended by Horn[‖] and Grittner.[¶] Five grammes of the sample are boiled, until thoroughly saponified, with 4 c.c. of 50 per cent. caustic soda solution and 100 c.c. of alcohol in a flask connected to a reflux condenser. The boiling-hot solution is poured into a basin, the flask well rinsed out with small quantities of boiling-hot alcohol, and the liquid evaporated to a small bulk over a steam-bath, with stirring. Some coarsely powdered pumice stone[**] is then added, and the contents of the basin are evaporated to dryness with continual stirring, so as to reduce the residue to small grains, and well dried in the steam oven. Any soap adhering to the basin is scraped off with a spatula, and the entire residue is transferred to a Soxhlet apparatus and extracted with chloroform, which is subsequently evaporated and the residue weighed. The basin is rinsed into the apparatus with hot chloroform before the extraction is commenced. Two hours' extraction, if the apparatus is working well, will dissolve all the alcohols from 5 grammes of saponified beeswax; only traces are extracted in the second hour.

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[*] Lewkowitsch, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 137; Herbig, *ibid.*, xiii. (1894), p. 1068.

[†] For 5 grms. of fat use 4 c.c. of 50 per cent. caustic soda solution diluted to 25 c.c. with absolute alcohol.

[‡] This must be pure rubber, free from substitutes.

[§] Allen, *Comm. Org. Anal.*, vol. ii. pt. i. p. 49.

[‖] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 696.

[¶] *Ibid.*, ix. (1890), p. 772.

[**] The fragments of pumice should pass through a sieve having 11 meshes to the linear inch, and should contain no powder which will pass a 24 mesh sieve.

Sufficient pumice must be added to enable a granular non-pasty residue to be obtained. Sand, which is sometimes recommended, is less suitable than coarse pumice and must, according to Grittner, be purified from calcium carbonate by washing with hydrochloric acid, in order to prevent the formation of lime soaps which are soluble in chloroform. Chloroform is used in preference to petroleum ether, as it does not dissolve the soda soap. It is, however, desirable to make sure that the unsaponifiable matter is free from soap by determining the ash of a portion, as recommended by Lewkowitsch. It is also desirable before evaporating the soap solution to add sufficient sodium bicarbonate to convert the excess of caustic soda into carbonate (2·1 grammes $NaHCO_3$ for 1 gramme NaOH). If petroleum ether be used this is essential.

II. Estimation of Small Quantities of Saponifiable Matter in Mineral Oils.

In the analysis of mineral oils containing small quantities of fat or resin, it is preferable to determine the fatty or resin acids, as described in section G. (p. 224), and estimate the hydrocarbon oil by difference. The percentage of fatty acids obtained, divided by 0·95, will give approximately the percentage of fatty oil.

F.—COMPOSITION AND IDENTIFICATION OF UNSAPONIFIABLE MATTERS.

The unsaponifiable matter obtained in the analysis of lubricants may be expected to contain—

Hydrocarbons; including **Mineral oil** from petroleum or shale. **Rosin oil.** (**Neutral tar oil** from coal tar). **Hydrocarbons** from distilled wool grease.	Liquid at the ordinary temperature.
Paraffin wax or cerasin. **Vaseline.** **Wax Alcohols**, from sperm oil, wool fat, etc. **Cholesterol and isocholesterol**, from wool fat, liver oils, etc. **Phytosterol**, from vegetable oils. *Colouring matter* (*traces*). *Unsaponified fat or oil.* *Soap.*	Solid or semi-solid at the ordinary temperature.

I. **Hydrocarbons**, whether liquid or solid, may be identified by their sparing solubility in alcohol. If a small drop of the unsaponifiable matter on the end of a thin glass or platinum rod, or in a platinum wire loop, be immersed in a little cold rectified alcohol in a test tube which is held up between the eye and a window, pure hydrocarbon oil will shew no sign of solution, and the drop will probably appear fluorescent at the edges; but if wax alcohols from sperm oil be present they will quickly dissolve and cause visible stream lines in the liquid. If the unsaponifiable matter be solid the solvent alcohol may be gently warmed, sufficiently to melt it.

(*a*) *Fluorescence* is a very characteristic property of hydrocarbon oils, though all do not shew it. Distinct fluorescence of the unsaponifiable matter or of its ethereal solution proves the presence of hydrocarbons; but a non-fluorescent appearance does not prove their absence. If the fluorescence be not readily observed, Allen recommends laying a glass rod, previously dipped in the oil, on a table in front of a window, so that the oily end of the rod projects over the edge of the table away from the window and can be seen against the dark background of the floor. Another plan is to make a broad streak of the oil on a piece of black marble, or on a sheet of glass lying on black paper or cloth. The fluorescence of hydrocarbon oil is, as a rule, greatly intensified by solution in ether, which frequently leads to its detection while the unsaponifiable matter is being extracted. Mineral oils which have been 'debloomed' by chemical treatment (see p. 94) regain their fluorescence by treatment with an equal measure of strong sulphuric acid (*Allen*).

(*b*) Hydrocarbon oils are unacted upon when submitted to the *acetylation test* (p. 231). If the unsaponifiable matter after treatment with acetic anhydride has no saponification value, hydrocarbons alone are present.

(*c*) If the unsaponifiable matter consist entirely of hydrocarbons, the *specific gravity* should be determined by the alcohol method (p. 170). Mineral lubricating oils (including also vaseline and paraffin wax) vary in specific gravity from about 0·850 to about 0·920 at 60° F.; rosin oil is heavier, ranging from about 0·96 to 0·99; tar oils exceed 1·0 in specific gravity and will therefore sink in water. For the examination of mixtures see section S. (p. 284).

(*d*) **Vaseline** at the ordinary temperature is semi-solid, soft, and amorphous; **paraffin wax** is more or less hard and crystalline. Allen has shewn that although in the solid state these substances are nearly of the same specific gravity, their densities in the liquid state at the temperature of boiling water are widely different; his results are summarized in the following table:—

Description.	Specific Gravity.	
	Solid, at $\frac{15·5°}{15·5°}$ C.	Melted, at $\frac{99°}{15·5°}$ C.
Vaseline (9 samples), . . .	0·856–0·909	0·804–0·855
Paraffin wax (7 samples), . .	0·867–0·911	0·748–0·757

Allen's results at 99° were obtained with the Westphal balance, and as no correction was made for the expansion of the plummet, they are about 0·002 too high (*Alder Wright*).

(*e*) Mineral oils absorb variable amounts of *iodine*, according to the proportion of unsaturated hydrocarbons contained in them. Paraffin wax and cerasin absorb less than 5 per cent. of iodine, vaseline absorbs rather more, and the fluid oils absorb up to 23 per cent. (see Table LXIX., p. 246). Rosin oils absorb from 43 to 48 per cent. (*Valenta*).

II. **The Wax Alcohols** which most frequently occur in lubricants are those derived from *sperm or bottlenose oil.* Their nature is at present unknown. When obtained from pure sperm or bottlenose oil, they are crystalline and almost colourless, having only a very pale greenish yellow tint. Their consistence at the ordinary temperature is that of solid, soft fat, and they melt at 23·5° to 27·5° C. They dissolve easily in warm rectified alcohol, and the solution remains clear on cooling; if, therefore, the 'unsaponifiable matter' from 5 grms. of oil is completely soluble in about 2 c.c. of cold rectified spirit it cannot contain an appreciable quantity of hydrocarbons, and probably consists entirely of the mixed alcohols from sperm or bottlenose oil. These alcohols may be further identified by their iodine value, 60–70 per cent.; by their specific gravity at $\frac{100°}{100°}$ C., about 0·827; and by the acetylation test described on p. 231. When mixed with twice their volume of acetic anhydride, they dissolve easily when gently warmed, and the solution remains clear on cooling; the mixed acetates have a saponification value of 18·55 per cent., according to one experiment.

III. **The Mixed Alcohols from Wool Fat** are pale yellow, have the characteristic odour of wool fat and the consistence of wax. Melting point, 44°–48° C. Iodine value, about 35–40 per cent. Specific gravity at $\frac{100°}{100°}$ C., about 0·957. They dissolve readily in warm rectified alcohol; but on cooling even a dilute solution, partial precipitation occurs. By fractional crystallization from a hot, strong solution in alcohol or ether-alcohol, crystals of cholesterol are obtained, which may be identified by their melting-point, crystalline form, and colour reactions (see p. 281). The mixed acetates formed by boiling the alcohols with acetic anhydride require from 15·3 to 16·1 per cent. of potash for saponification. These properties easily distinguish the wool fat alcohols (when pure) from those of sperm and bottlenose oils.

IV. **Beeswax and Carnauba Wax** are unlikely to occur in the analysis of lubricants, though the latter is said to be used in the manufacture of a particular description of palm soap used for making railway wagon grease. The presence of either wax could scarcely fail to be indicated by the insoluble character and comparatively high melting-point of the myricyl alcohol formed by saponification. This alcohol, mixed in the case of beeswax with some hydrocarbons, is the chief constituent of the 'unsaponifiable matter' of both waxes; it is white or pale yellow in colour, very hard and brittle, soluble with difficulty in even boiling alcohol and almost entirely crystallizes out on cooling. Melting-point of the products from beeswax, 76° (owing to the hydrocarbons present), and from carnauba wax, 85°. Saponification value of the mixed acetates from beeswax, 10 per cent., and from carnauba wax, 12 per cent.

V. **Cholesterol and isocholesterol** form a large proportion of the unsaponifiable matter of wool fat. Cholesterol also occurs in smaller quantity in liver oils (shark liver oil, cod liver oil, etc.) and is characteristic of animal oils generally. On the other hand, a very similar substance, **phytosterol**, the 'cholesterol of plants,' is found in the unsaponifiable matter of rape oil and of most if not all other vegetable seed oils, and olive oil. All three substances are monatomic alcohols of the aromatic series, generally regarded as isomeric, and having the formula $C_{26}H_{44}O$. They are colourless and tasteless crystalline bodies, of high melting-point, insoluble in water, sparingly soluble in cold alcohol, but easily soluble in hot alcohol, ether, and chloroform. They may be distinguished, when in a pure state, by their melting-points and crystalline forms, which are given in the following table:—

TABLE LIX.

	Cholesterol.	Isocholesterol.	Phytosterol.
Melting-point (corrected), °C.	148–148 (*Bömer.*)	137–138	135·5–141 (*Bömer.*)
Crystalline form.	Thin rhombic plates of $C_{26}H_{44}O$. aq. from hot alcohol and ether. —— Anhydrous needles from chloroform.	Flocks from dilute alcohol: a jelly from concentrated alcoholic solution: needles from ether.	Tufts of needles. $C_{26}H_{44}O$. aq. from hot alcohol; anhydrous needles from ether and chloroform.

According to Bömer,* cholesterol and phytosterol when present together cannot be separated by crystallization.† The melting-point of the mixture in general approximates to that calculated from the mean proportions of its components. The mixture crystallizes in one form only, the crystals either approximating in form to phytosterol crystals or, if cholesterol be present in the greater proportion, differing in form from the crystals of either body.

To obtain the crystals, the unsaponifiable matter from 50 grms. of fat should be boiled with a small quantity of alcohol and the solution filtered hot. The crystals deposited on cooling must then be purified by repeated re-crystallization, and examined under the microscope. They should be compared with the crystals obtained in the same way from pure samples of, say, rape oil (phytosterol), cod liver oil (cholesterol), and wool fat (cholesterol and isocholesterol). (Compare Salkowski, *Jour. Chem. Soc.*, 1888, Abs. 201.)

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* [illegible] 1898, pp. 42 and 532; Jour. Soc. Chem. *Ind.*, xvii. (1898), p. [illegible]

† Compare Lewkowitsch, Jour. Soc. Chem. *Ind.*, xviii. (1899), p. 557.

Cholesterol gives several characteristic colour reactions (see p. 281) which distinguish it from isocholesterol, but not from phytosterol which gives the same reactions.

VI. **Unsaponified oil or fat** will not occur in more than traces if the saponification has been properly carried out, and **Soap** should not occur at all. If there be any reason to suspect the presence of either, the ether residue must be purified by boiling it with alcoholic soda (say 2 c.c. 50 per cent. NaOH solution and 25 c.c. alcohol) under a reflux condenser for half-an-hour and re-extracting with ether after evaporating off alcohol and diluting with water. If wool fat be suspected, the re-saponification must be conducted under pressure with alcoholic soda of double normal strength.

TABLE LX.—PERCENTAGE OF UNSAPONIFIABLE MATTER OBTAINED FROM FIXED OILS, FATS, AND WAXES.

NAME OF OIL, ETC.	UNSAPONIFIABLE MATTER, PER CENT.	
Olive oil,	0·75– 1·50	Under 2 per cent.
Arachis oil,	0·54– 0·94	
Castor oil,	0·30– 0·37	
Palm oil,	1·25	
Rape oil,	0·58– 1·30	
Ravison oil,	1·45– 1·66	
Cottonseed oil,	1·07– 1·85	
Maize oil,	1·35– 1·55	
Linseed oil,	0·60– 1·28	
Hempseed oil,	1·00	
Poppyseed oil,	1·15	
Tallow,	0·50	
Lard,	0·23– 0·30	
Seal oil,	0·38– 0·51	
Menhaden oil,	1·60	
Sardine oil,	0·56– 1·44	
Whale oil,	0·65– 3·7	Over 2 per cent.
Cod liver oil,	0·46– 2·68	
Shark liver oil,	0·93– 5·27 (*Fahrion*) 0·70–17·3 (*Allen*)	
Sperm oil,	36·3 –41·5	
Arctic sperm oil,		
Crude wool fat,	Very variable; 35 to 40 % is usual.	
Beeswax,	52·3 –55·3	
Carnauba wax,	52·4 –55	
Spermaceti,	51·5	

TABLE LXI.—PROPERTIES OF THE MIXED ALCOHOLS, ETC. ('UNSAPONIFIABLE MATTER') OBTAINED FROM WAXES.

NAME OF WAX, ETC.	PROPERTIES OF MIXED ALCOHOLS, ETC.				Saponification Value of the Mixed Acetates, per cent.
	Melting Point, °C.	Specific Gravity at $\frac{100°}{100°}$ C.	Iodine Value.	Increase of Weight on Acetylating, per cent.	
Sperm oil, . . Arctic sperm oil, .	23·5°–27·5°	0·8271	59·5–69·3	15·7	18·55
Wool fat, . . .	44°–48°	0·9566	39·4	12·2–12·7	15·3–16·1
Beeswax, . . .	75°–76°	0·8239	..	6·5– 7·7	9·9–10·3
Carnauba wax, . .	85°	0·4826	..	10·2	12·3
Cholesterols (*theory*),			68·3	11·3	13·55
,, (*experimental results by Lewkowitsch*),			67·7		13·5

Note.—Many of the results in this table were obtained by Archbutt with single samples of the waxes in question, and therefore require confirmation.

G.—ESTIMATION AND IDENTIFICATION OF THE SAPONIFIABLE OIL IN MIXED OILS.

In the analysis of lubricating oils consisting of a mixture of mineral oil and fixed oil, it is usually sufficient to estimate the saponifiable oil by difference. But it is often necessary to liberate the fatty acids from the soap solution, in order to identify the fixed oil, and this may easily be done quantitatively, giving a number from which the percentage of fixed oil can be calculated. The details of manipulation are a continuation of the process for estimating the total unsaponifiable matter. (E. p. 215.)

The soap solution, which has been freed from mineral oil and other unsaponifiable matter by shaking three successive times with ether, is mixed with the first two aqueous washings of the mixed ethereal liquids and treated with a sufficient excess of dilute sulphuric acid to decompose the soap and liberate the fatty acids. The acid liquid is mixed with 50–70 c.c. of ether, well shaken in the separator, and, after allowing sufficient time for the ether to rise, the aqueous portion is drawn off into another separator where it is again shaken with ether. The ethereal liquids are mixed together in one separator, thoroughly washed by shaking six times with 10 c.c. of pure water each time, then poured into a tared flask, and the bulk of the ether is distilled off. The flask is then placed on the top of the water oven and heated until all water and ether have evaporated and the weight remains practically constant.

In the absence from the original sample of the following:—

Sperm and bottlenose oils,
Porpoise and dolphin jaw oils,
Shark liver oil,
Palm nut and coconut oils,
Wool fat,
Blown oils,
Soap,
Resin,
Free fatty acids,

the percentage of fatty acids obtained, ÷ 0·957, will give approximately the percentage of fatty oil in the sample. Fatty acids existing in the original sample, either in the free state or as soap, must previously be separated as described in the analysis of greases (p. 317). Resin acids, if present, must be determined by Twitchell's process (p. 228) and the amount deducted.

If the saponifiable oil consist entirely of blown rape or cottonseed oil the divisor becomes approximately 0·85 instead of 0·957, but special washing with hot water is required to remove the soluble fatty acids (see p. 226). In the presence of sperm oil and wool fat the problem becomes more complicated. The unsaponifiable matter in that case contains wax alcohols, and must be analysed by the acetylation process (p. 233).

As there is no known means of separating, without decomposition, a fixed oil or fat from a heavy mineral oil, the identification of the fatty oil in such mixtures depends upon the identification of the mixed fatty acids. For this purpose, the following determinations are available:—

1. *The melting-point* (table on p. 197).
2. *The sp. gr. at* $\frac{100^\circ}{100^\circ}$ *C.* (table on p. 177).
3. *The iodine value* (table on p. 245).
4. *The saponification or neutralization value.*

The fatty acids used for the determination of the iodine value must not have become oxidized, otherwise a low result will be obtained. After distilling off the ether the flask should, therefore, be closed by means of a cork carrying two tubes, in order that a current of dry carbon dioxide gas may be passed through the flask while heating on the steam-bath.

The saponification or neutralization value is best determined in the same manner as the saponification value of an oil or fat (p. 211), viz.:—by heating 2·5 grms. with approximately semi-normal alcoholic potash in excess, and titrating back with accurate semi-normal hydrochloric acid. Theoretically, it should be sufficient to dissolve the fatty acids in alcohol and neutralize with standard potash solution in the cold, but if any undecomposed ethers are present, a low result is obtained unless the potash be in excess and the liquid heated.

In the absence of soluble fatty acids, the neutralization value of the mixed fatty acids multiplied by the Hehner value of the oil will give the saponification value of the oil, *i.e.*, the neutralization value × 0·957 will give, approximately, the saponification value of the oil or fat from which the fatty acids have been derived.

H.—INSOLUBLE FATTY ACIDS (HEHNER VALUE).

The process for determining the *total fatty acids* described in the preceding section (p. 224) is based upon the assumption that they are entirely, or almost entirely, insoluble in water and non-volatile, and such is, as a rule, the case. A few oils and fats, however, contain a considerable proportion of soluble and volatile fatty acids, notably cow's butter, dolphin jaw oil, and porpoise jaw oil. In such cases, the insoluble acids must be determined by a special process. Hehner was the first to shew that the percentage of insoluble fatty acids contained in genuine butter fat is fairly constant, and that by its determination the adulteration of butter with foreign fats can be detected; the percentage of insoluble fatty acids contained in an oil or fat is therefore known as the '*Hehner Value.*'

It has been shewn by Fox and Baynes* and by Thomson and Ballantyne† that the changes caused by 'blowing' oils include a partial conversion of the insoluble acids into soluble and volatile acids; the presence, therefore, of 'blown' oil in castor oil would be indicated by a reduction of the percentage of insoluble fatty acids, of which genuine castor oil contains upwards of 95 per cent.

To determine the Hehner Value of a fixed oil or fat, the fatty acids must be washed with boiling water until the washings are no longer acid. The following is a convenient method of operating:—Saponify 5 grms. of the oil with alcoholic soda, as directed in E. I. (p. 215), and after saponification is complete, evaporate to dryness over a steam-bath, and heat to remove alcohol. Dissolve the soap in hot water, and rinse the solution into a beaker-flask, the total volume being about 250 c.c. Liberate the fatty acids with dilute sulphuric acid, allow to stand on the steam-bath until the fatty acids have melted to a clear layer upon the surface of the liquid, then pour the whole carefully into a separating funnel previously rinsed with hot water. Support the separator over a wet filter paper contained in a jacketed hot water funnel, and allow the clear liquid to run into the filter at a sufficient speed to keep it nearly full. The filtrate should be bright. Do not allow the oily layer to pass on to the filter, but return it to the original beaker-flask, and having added about 150–200 c.c. of boiling water, thoroughly churn the fatty acids and water together by circular agitation. Allow to stand again until the acids have risen, carefully decant into the separator, and run the aqueous portion through the wet filter as before. Repeat this washing five times more, but collect the last washing in a separate vessel, add a few drops of phenolphthalein solution, and find how much decinormal soda is required to produce a pink colour. Make a similar experiment with the same quantity of the hot distilled water used in washing the fatty acids. If practically the same number of drops are required in both experiments (disregard a difference of one or two drops) the washing is complete. When this is the case, allow the insoluble fatty acid layer to pass on to the filter paper, and let the water drain away; well drain, also through the filter, the separator and the beaker-flask. So long as the paper remains thoroughly wet the fatty acids will not run through the paper. Transfer the wet filter paper containing the fatty acids to a dry funnel supported over a small weighed beaker, and place it in the water-oven until the filter has dried and the greater part of the fatty acids have drained through into the beaker. Then place the funnel containing the oily filter paper over a weighed flask, and, when cold, thoroughly wash the paper with ether, allowing the latter to run into the flask, also rinse the separating funnel and the beaker-flask * with ether, passing the liquid through the same filter paper. Then distil off the ether, and heat both the flask and the small beaker until constant in weight. Deduct the weight of the two vessels, and the difference is the weight of the insoluble fatty acids.

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* *Analyst*, xii. (1887), p. 33. † *Jour. Soc. Chem. Ind.*, xi. (1892), p. 506.

In the presence of hydrocarbons or waxes, the soap solution obtained by saponification must first be extracted with ether, as described in E. I. (p. 215), then poured into a basin, gently heated over a steam-bath, with a cover on the basin, to expel the dissolved ether, thoroughly boiled to evaporate the alcohol, and then acidified and treated as described above.

Qualitative Preparation of Insoluble Fatty and Resin Acids.—If it be required merely to prepare the insoluble fatty and resin acids, without making a quantitative estimation, the following method may be employed:—Saponify in a basin, by thorough boiling with alcoholic soda, a roughly weighed quantity of the oil, sufficient to give rather more than the required quantity of fatty acids, using for every 5 grms. of oil 2 grms. of caustic soda (4 c.c. of a 50 per cent. solution). Dissolve the soap in boiling water, and boil until alcohol is expelled. Add sufficient dilute sulphuric acid to liberate the fatty acids, gently boil until they form a clear layer on the surface of the liquid, then, by means of a large pipette with a flexible mouthpiece, draw off the watery fluid. Boil the fatty acids in the basin several times with water, drawing off the water with the pipette each time, then pour them on to a wet filter contained, if necessary (*i.e.*, if the fatty acids have a high melting-point), in a hot water funnel, and wash with boiling water until the washings are practically neutral to litmus or phenolphthalein. Pierce the filter, collect the acids in a dry beaker, and heat in the water-oven until quite clear and free from visible water.

Table LXII. (p. 228) contains the Hehner values of most oils and fats which are likely to occur in lubricants.

I.—ESTIMATION OF ROSIN (COLOPHONY).

The fatty acids obtained by either of the processes described in sections G and H include the resin acids, if rosin be present. If an estimation of the rosin be desired, Twitchell's process † is the best to adopt. It depends upon the fact that when a solution of fatty acids in absolute alcohol is saturated with hydrochloric acid gas

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* These may be previously dried by placing them on the water-oven, or they can be rinsed with ether while wet.

† *Jour. Soc. Chem. Ind.*, x. (1891), p. 804.

TABLE LXII.—HEHNER VALUES.

NAME OF OIL OR FAT.	HEHNER VALUE. Percentage of Insoluble Fatty Acids.
Most vegetable and terrestrial animal oils and fats, except wool fat,	95–97 Average about 95·7
Palm nut oil,	91·1
Coconut oil,	83·8–90·5
Marine animal oils, except sperm and shark liver, but including porpoise body and dolphin body oils,	92·8–95·5 Average about 94·1
Porpoise jaw oil,	68·4 and 72·1
Dolphin jaw oil,	66·3
Blown rape oil,	84·7
„ cottonseed oil,	85·5 [*]
„ linseed oil,	86·7
„ seal oil,	73·4

the ethyl esters of fatty acids are formed. Resin acids similarly treated in the cold are practically unacted upon, and can be separated from the esters by treatment with weak caustic soda solution in the cold, which dissolves the resin acids, the esters remaining insoluble. The details of the process are as follow:—

From 2 to 3 grms. of the melted mixture of fatty and resin acids are poured into a dry tared conical flask of about 8 ozs. capacity, and, when cold, the weight is accurately ascertained. The acids are dissolved in absolute ethyl alcohol,[†] using 10 c.c. for every gramme of acids, and dry hydrochloric acid gas, in a moderate stream, is passed through the solution until saturated, the flask being kept quite cold by immersion in a basin of cold water.[‡] The hydrochloric acid gas may be prepared in a dry state by acting upon lumps of fused salt with concentrated sulphuric acid, and may then be passed direct into the liquid. The gas is rapidly absorbed, and the esters separate in oily drops. When the alcoholic liquid is saturated (from 30–45 minutes are required), the flask is allowed to stand about half-an-hour longer to ensure complete etherification. It must not stand too long, otherwise low results are obtained. The liquid is then diluted with about five times its volume of boiling water, and heated on the steam-bath until some of the alcohol has evaporated and the esters, with the resin acids in solution, form a clear layer upon the surface. The contents of the flask are poured into a separating funnel, and the flask as well as the gas delivery tube are rinsed with ether, which is poured into the separator. About 50 c.c. more ether are added, the contents of the separator are cooled, well shaken, and allowed to stand for the ether to rise. The acid liquid is drawn off into another separator and shaken again with a little ether, which is added to the first, and the ethereal solution is then washed once with about 10 c.c. of cold water, which is drawn off. It is then shaken in the funnel with 50 c.c. of dilute caustic soda solution containing 1·0 grm. of caustic soda and 10 c.c. of alcohol in 100 c.c., by which the resin acids are immediately saponified and dissolved. After drawing off the alkaline liquid into a second separator, the ethereal solution is again shaken with about 20 c.c. more of the weak soda solution, which is added to the first, and the whole is then decomposed with dilute sulphuric acid and shaken with ether to dissolve the liberated resin acids. The ethereal solution, after washing several times with small quantities of cold water, is run through a dry filter paper into a weighed flask, the ether is evaporated, and the residual resin acids are heated in the water-oven until constant in weight. They should be quite hard and brittle. The weight obtained, multiplied by 100 and divided by the weight of mixed acids taken, gives the percentage of resin acids.

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[*] Fox and Baynes; mean results.

[†] Methyl alcohol is said to give lower results than ethyl alcohol.

[‡] Evans and Black recommend the use of a tall cylinder surrounded by iced water. Temperature must not rise above 20° C., nor must the stream of hydrochloric acid be too rapid, otherwise low results are obtained. *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 689; also *Analyst*, xx. (1895), p. 60.

Lewkowitsch,* who has extensively investigated this process, finds that the amount of resin acids generally falls short of the truth. Evans and Black, however, state that the percentage of resin acids is correctly estimated, and that the loss is due to unsaponifiable matter contained in rosin which is not dissolved by the caustic soda solution. Six samples of rosin were found by them to contain from 5·0 per cent. to 9·71 per cent. of gummy matter unsaponifiable by alcoholic potash.

J.—VOLATILE FATTY ACIDS (REICHERT AND REICHERT-MEISSL VALUES).

The Reichert Process.—As has already been stated, a few oils and fats yield a considerable proportion of fatty acids soluble in water, and when the liquid is distilled these fatty acids are usually found in the distillate. By distillation in a current of steam, complete separation of the volatile and non-volatile acids can be effected,† but the process is tedious. In Reichert's process only a portion of the volatile acids are distilled over, but by working under strictly defined conditions uniform results are obtained.

In the process as originally described,‡ 2·5 grammes of the fat were saponified with an alcoholic solution of caustic soda, the alcohol was completely evaporated off, the soap dissolved in 50 c.c. of water, decomposed by adding 20 c.c. of dilute sulphuric acid and distilled until exactly 50 c.c. had come over. The distillate was then mixed with a few drops of litmus solution and titrated with decinormal alkali, the number of cubic centimetres required being recorded. Under these conditions, the distillate from cow's butter required not less than 13 c.c. of decinormal acid for neutralization, while the fats used in the manufacture of artificial butter required less than 0·5 c.c.

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* *Jour. Soc. Chem. Ind.*, xii. (1893), p. 503.

† Goldman, *Chem. Zeit.*, 1888, xii. p. 183 ; xiv. p. 216 ; xx. p. 317 ; *Jour. Soc. Chem. Ind.*, vii. (1888), pp. 238 and 348. Beal, *Jour. Amer. Chem. Soc.*, xvi. (1894), p. 673 ; *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 197.

‡ *Zeits. f. Anal. Chem.*, xviii. p. 68.

The Reichert-Meissl Process.—Reichert's process has undergone a variety of modifications in detail,* and as now carried out saponification is generally effected with a mixture of caustic soda solution and glycerin (*Leffmann and Beam*), by which the evaporation of alcohol is avoided; also 5 grammes of fat are used instead of 2·5 grammes (*Meissl*), by which the volume of standard acid used in titrating is nearly, but not quite, doubled. This process, which is chiefly used in the analysis of butter, is required in the analysis of such lubricants as porpoise oil; it may also find occasional application in the detection of blown oils. The following reagents are required:—

1. *Glycerol-Soda.*—Made by mixing together 30 c.c. of aqueous caustic soda solution, containing 50 grammes NaOH in 100 c.c., and 170 c.c. of pure concentrated glycerin. This reagent is kept in a bottle closed with a rubber stopper.
2. *Dilute Sulphuric Acid.*—30 c.c. of pure concentrated sulphuric acid diluted with distilled water to 100 c.c.
3. *Decinormal Sulphuric Acid*, accurately standardized.
4. *Caustic Soda Solution* of approximately decinormal strength. A 10 c.c. pipetteful of this solution must be tinted with phenolphthalein and the strength determined by titration with the decinormal sulphuric acid.
5. *Phenolphthalein Solution.* (See p. 207.)

To determine the Reichert-Meissl value, a dry conical flask of 300 c.c. capacity is counterpoised on the balance. As nearly as possible 5 grammes of the oil or melted fat are dropped into the flask and the exact weight taken (in the case of a melted fat after becoming quite cold). 20 c.c. of the glycerol-soda are added, and the flask is heated over an Argand-Bunsen flame turned rather low. The liquid will foam, and to control this and hasten the operation the flask is frequently agitated. Heating and agitation are continued until practically all the water has been driven off, which will take about ten minutes; saponification will then be complete, and the flask is withdrawn from the flame and the soap dissolved by adding 135 c.c. of cold water. The first portions of water should be added drop by drop, and the flask shaken between each addition to avoid violent foaming. When the soap is dissolved, 5 c.c. of the dilute sulphuric acid are added, a few small fragments of pumice are dropped in, and the liquid is distilled until 110 c.c. have been collected. The tube connecting the flask to the condenser should have a large bulb to arrest the splashings and return them to the flask. The condensing tube should be of glass, and the rate of distillation such that the above amount of distillate is collected in about 30 minutes.

The whole of the distillate, if clear, is mixed with about 0·5 c.c. of phenolphthalein solution, and as many 10 c.c. pipettefuls of the standard caustic soda solution are added as are required to produce a strong crimson coloration; the liquid is then carefully titrated with decinormal sulphuric acid until the crimson colour is just discharged.

The distillate, if not clear, is passed through a dry ribbed filter, and 100 c.c. of the clear filtrate are titrated; in this case the volume of decinormal soda neutralized is increased by one-tenth.

A blank distillation must be made to determine the amount of decinormal soda required by the materials employed; with a good quality of glycerin this will not exceed 0·5 c.c.

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* For a full account, see Richmond, *Analyst*, xvii. (1892), p. 171.

EXAMPLE.

5 grms. of blown rape oil gave 110 c.c. of distillate, which was filtered. 100 c.c. of the filtrate were mixed with 10 c.c. of standard caustic soda solution, and 4·76 c.c. of decinormal H_2SO_4 were required for neutralization.

10 c.c. of standard soda required, . .	9·78 c.c. $\frac{N}{10}$ H_2SO_4
Deduct, ...	4·76 c.c.
Difference = volume of decinormal alkali required for 100 c.c. of distillate, . .	5·02
+ $\frac{1}{10}$th, . .	·50
∴ Volume required for 110 c.c., . .	5·52
Deduct for blank experiment, . . .	·40
Reichert-Meissl value (*volume of decinormal alkali required for 5 grammes of oil*), .	5·12

The Reichert process is used most extensively in the analysis of butter fat, 5 grms. of which, when genuine, yield a distillate requiring from 24 to 34 c.c. of decinormal alkali. Results obtained with other oils are given in Table LXIII. (p. 232).

The numbers in the first column were obtained chiefly by Allen and Moore, those in the second column are by Thörner, Holde, Archbutt, and others. It will be seen that the process is chiefly of value in the analysis of (besides butter fat) porpoise and dolphin oils and croton oil. It would not be of much service for the detection of blown oils, unless these were present in large quantity.

K.—ACETYLATION TEST (THE ACETYL VALUE).

The action of acetic anhydride (acetyl oxide) upon alcohols and hydroxylated fatty acids is applied in the analysis of lubricants both in the examination of unsaponifiable matter containing or suspected to contain wax alcohols and also in the analysis of castor oil.

I. Acetylation of Alcohols.—When the alcohols are heated with acetic anhydride they are converted into acetates (esters), the hydrogen of their hydroxyl group or groups being replaced by acetyl, C_2H_3O. Thus, in the case of cetyl alcohol (from spermaceti), the following reaction takes place:—

$$\underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH} + \underset{\text{Acetic anhydride}}{(C_2H_3O)_2O} = \underset{\text{Cetyl acetate}}{C_{16}H_{33}O.C_2H_3O} + \underset{\text{Acetic acid}}{C_2H_4O_2}$$

Glycerol, $C_3H_5(OH)_3$, is similarly converted into tri-acetin, $C_3H_5(OC_2H_3O)_3$, but this reaction does not interest us here since

glycerol does not occur in the 'unsaponifiable matter.' Hydrocarbonsare unacted upon. In the case of the monohydric alcohols and cholesterol, the esters formed are crystalline bodies, insoluble in water, and can be washed free from acetic acid and weighed. The saponification

TABLE LXIII.

Description of Oil, etc.	Reichert Value =c.c. of N/10 Alkali required for 2·5 grms.	Reichert-Meissl Value =c.c. of N/10 Alkali required for 5 grms.
Olive oil,	...	0·45–1·5
Arachis (earthnut) oil,	...	0·4
Castor oil,	1·4	2·2 –4·0
Croton oil,	...	13·4
Palm oil,	0·5 – 0·8	0·6
Palm nut oil,	2·4	3·4 –5·0
Coconut oil,	3·5 – 3·7	7·3 –7·5
Rape oil,	0·25– 0·4	0·4 –0·9
Cottonseed oil,	0·3	0·95
Curcas oil,	...	0·28–0·48
Sesamé oil,	0·35 (2·2)	1·2
Maize oil,	0·33	...
Linseed oil,	...	0·9
Poppyseed oil,	...	0·6
Sunflower oil,	...	0·5
Tallow,	0·25	1·0 –1·2
Horse fat,	0·3 – 0·4	1·6 –2·1
Lard,	...	1·1
Sperm oil,	1·3 – 1·4	...
Porpoise body oil,	11–12 (*Allen*)	46·9 (*Steinbuch*)
Porpoise jaw oil (skimmed and strained),	47·8 –56·0 (*Moore*)	131·6 („)
Porpoise jaw oil (unstrained),	2·1	...
Dolphin body oil,	5·6	...
Dolphin jaw oil (skimmed and strained),	65·9	...
Whale oil,	0·7 –12·5	...
Seal oil,	0·07–0·22	...
Menhaden oil,	1·2	...
Cod liver oil,	0·2 (1·1-2·1)	0·1 –0·4
Wool fat (crude),	...	6·5
Blown East India rape oil,	...	5·26
„ ravison oil,	...	5·43
„ cottonseed oil,	...	7·06

values of these esters are characteristic, and afford a means of identifying the waxes, as well as a method of estimating the proportion of a single known wax, such as sperm oil or wool fat, in a mixture containing hydrocarbons. The process is carried out as follows:—

A quantity of not less than 2–3 grms. of the unsaponifiable matter is boiled with acetic anhydride in a small flask under a reflux condenser for half an hour. If the *yield* of acetates is to be determined, the weight of the substance taken must be exactly known, and the flask must also be tared. 1 c.c. of acetic anhydride per grm. of substance is sufficient, but if the available weight of substance be small, 2 c.c. per grm. may be used, in order to give a sufficient quantity of liquid to boil. If the unsaponifiable matter consist chiefly of alcohols, it will dissolve completely in the hot liquid; but if a considerable proportion of hydrocarbons are present, they will float on the liquid, and may give rise to explosive ebullition; in this case a few small fragments of ignited pumice stone should be dropped into the flask.

The contents of the flask are next diluted with boiling water and heated over the steam-bath, with frequent agitation, for a few minutes, in order to convert the unchanged acetic anhydride into acetic acid, which dissolves in the water, and to allow the esters, together with hydrocarbons if present, to rise and float upon the surface as an oily layer. The hot liquid is next poured upon a wet filter, and if it be desired to ascertain the weight of the acetylated product the flask is thoroughly rinsed on to the filter with small quantities of boiling water, until free from acetic acid; it is then placed in the water-oven to dry. The oily liquid in the filter is thoroughly washed with boiling water, until the washings are perfectly neutral, and the filter is then placed in a dry funnel over the flask in the water-oven until the acids have run through. The oil absorbed by the filter paper is (after cooling) rinsed into the flask with ether (or with boiling chloroform if myricyl alcohol is present), the solvent is evaporated off, and the residue is weighed constant. The saponification value is then determined in the usual way on 2·5 grms., or the whole quantity may be used if not exceeding 2·5 to 3 grms. in weight.

Table LXIV. (p. 234) contains the results obtained by treating in this way the unsaponifiable matter (mixed alcohols) from sperm oil, wool fat, beeswax, and carnauba wax; also the results theoretically yielded by some alcohols known to occur in fats and waxes.

The alcohols of sperm oil are unknown; according to Lewkowitsch they belong for the most part, if not wholly, to the ethylene series. The alcohols of wool fat are also partly unknown, but cholesterol and isocholesterol occur in them to a large extent, and ceryl alcohol also is present. Myricyl alcohol is the chief part of the unsaponifiable matter from carnauba wax and beeswax; in the latter hydrocarbons occur to the extent of 15–17 per cent., which accounts for the low saponification value of the acetylated product. Cetyl palmitate is the chief constituent of spermaceti, in which octadecyl alcohol also occurs.

Analysis of Mixtures containing Sperm Oil or Wool Fat and Mineral Oil.—(*a*) When a mixture containing sperm oil or wool fat and mineral oil is saponified, the unsaponifiable matter extracted from the soap solution by ether contains the whole of the mineral oil together with the mixed alcohols of the wax, and in order to determine the percentage of mineral oil directly the alcohols must be separated. No satisfactory method of doing this has yet been proposed. Both ordinary alcohol and acetic anhydride, even in the cold, dissolve not only the wax alcohols but also some of the mineral oil, and therefore the methods described by Horn[*] and Lobey de Bruyn[†] are not trustworthy.

(*b*) The percentage of sperm oil in a mixture containing nothing else except mineral oil could easily be calculated, with approximate accuracy, from the saponification value of the mixture; but when a second, perhaps unknown, fatty oil is present this method is not available. Assuming that the third constituent of the mixture is not another wax such as wool fat, or a liver oil containing much cholesterol, the problem can be solved by determining the percentage of total unsaponifiable matter, acetylating it, and determining the saponification value of the acetylated product. Taking the numbers for sperm oil given in the table above, and 38 as the percentage of mixed alcohols formed by the saponification, the percentages of mineral oil and sperm oil in the mixture can be calculated as follows:—

TABLE LXIV.—RESULTS OF THE ACETYLATION OF ALCOHOLS.

Alcohol.	Formula.	Formula of Acetate.	Yield of Acetate per 100 pts. of Alcohol (Theory).	Saponification Value of Acetate, per cent. (Theory).
Cetyl, . .	$C_{16}H_{33}OH$	$C_{16}H_{33}O.C_2H_3O$	117·35	19·76
Octadecyl, .	$C_{18}H_{37}OH$	$C_{18}H_{37}O.C_2H_3O$	115·55	17·99
Ceryl, . .	$C_{27}H_{55}OH$	$C_{27}H_{55}O.C_2H_3O$	110·61	12·81
Myricyl, .	$C_{30}H_{61}OH$	$C_{30}H_{61}O.C_2H_3O$	109·59	11·69
Cholesterol, .	$C_{26}H_{43}OH$	$C_{26}H_{43}O.C_2H_3O$	111·29	13·56

Unsaponifiable Matter (Mixed Alcohols, etc.), from	Yield of Mixed Acetates per cent. (Expt.).	Saponification Value of Mixed Acetates per cent. (Expt.).
Sperm oil, ...	115·71	18·55
Wool fat (crude), ...	112·21	16·06
„ (neutral),[‡]	112·7	15·63
„ „ [§]	108·3 (?)	15·32
Beeswax, ...	106·46	9·84
„ (another sample), ...	107·62	10·25
Carnauba wax, ...	110·17	12·14
Cholesterol (pure),[‖]	...	13·49

Let x = the percentage of total unsaponifiable matter yielded by the sample.

„ y = the percentage of KOH required for the saponification of the acetylated product.

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[*] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 696.

[†] *Ibid.*, xiii. (1894), p. 426.

[‡] Lewkowitsch, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 138.

[§] *Ibid.*, xv. (1896), p. 14.

[‖] *Ibid.*, xi. (1892), p. 143.

Then, $\frac{x \times y \times 100}{18{\cdot}55 \times 115{\cdot}71}$ = the percentage of mixed alcohols (a) yielded by the sample.

$x - a$ = the percentage of mineral oil.

$\frac{100\,a}{38}$ = the percentage of sperm oil.

To test the method, two mixtures of sperm oil and '885' pale mineral oil were prepared and analysed with the following results:—

1. *Mixture containing 2 pts. sperm oil, and 1 pt. mineral oil.*

		Per cent.
Weight taken; 5 grms.		
Unsaponifiable matter obtained, 2·9706 grms.	=	59·41
Saponification value of the acetylated product, } 9·05 %.		
$\frac{59{\cdot}41 \times 9{\cdot}05 \times 100}{18{\cdot}55 \times 115{\cdot}76}$	=	25·04
Mineral oil found,		34·37
„ taken,		33·33

2. *Mixture containing 2 pts. mineral oil and 1 pt. sperm oil.*

		Per cent.
Weight taken; 5 grms.		
Unsaponifiable matter obtained, 3·9892 grms.	=	79·78
Saponification value of the acetylated product, } 3·47 %.		
$\frac{79{\cdot}78 \times 3{\cdot}47 \times 100}{18{\cdot}55 \times 115{\cdot}76}$	=	12·89
Mineral oil found,		66·89
taken,		66·66

Buisine's process for estimating hydrocarbons in beeswax, which consists of heating the wax with potash-lime to 250° C., whereby the wax alcohols are converted into fatty acids and soaps, from which the unchanged hydrocarbons can be extracted by means of ether,* would be applicable to a mixture of sperm oil and mineral oil, but not to a mixture containing wool fat or cholesterol, since the latter remains practically unchanged (see Lewkowitsch, *Jour. Soc. Chem. Ind.*, 1896, p. 14).

II. Acetylation of Hydroxylated Fatty Acids and Glycerides.

Determination of the Acetyl Value.—The action of acetic anhydride on hydroxylated fatty acids is similar to its action upon alcohols, the hydrogen of the alcoholic hydroxyl group or groups being replaced by acetyl. Thus:—

$$\underset{\text{Ricinoleic acid}}{C_{17}H_{32}(OH)COOH} + \underset{\text{Acetic anhydride}}{(C_2H_3O)_2O} = \underset{\text{Acetyl-ricinoleic acid}}{C_{17}H_{32}(O.C_2H_3O)COOH} + \underset{\text{Acetic acid}}{C_2H_4O_2}$$

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* See Lewkowitsch, *Analysis of Oils, etc.*, p. 214.

Benedikt and Ulzer, believing that those fatty acids which contain no alcoholic hydroxyl, such as stearic, oleic, and all the more commonly occurring fatty acids, are unacted on by acetic anhydride, have proposed the following method for the valuation of castor oil:—

Benedikt's Method.—About 20 grms. of the insoluble fatty acids, prepared as directed on p. 227, are boiled with an equal volume of acetic anhydride for 2 hours in a flask connected to a reflux condenser. The contents of the flask are poured into a Jena glass beaker of 1 litre capacity and diluted with about 500 c.c. of boiling water; the beaker is then placed on a thin disc of asbestos millboard, and the liquid is boiled briskly for half-an-hour with a cover on the beaker. To prevent explosive ebullition, a slow current of carbon dioxide is conducted through the liquid by means of a piece of thermometer tube reaching nearly to the bottom of the beaker. The oil and water are allowed to separate, the aqueous liquid is siphoned off, and the oily layer is again boiled with water. After boiling in this way with three successive quantities of water, the oil is poured on to a wet filter and washed with boiling water until the washings are neutral. The filter containing the acetylated acids is then removed to a dry funnel, which is placed in the water-oven over a dry beaker and left until the acids have run through.

2·5 grms. of the dry acetylated acids thus prepared are weighed into a small flask, dissolved in about 10 c.c. of neutralized rectified alcohol, mixed with a few drops of phenolphthalein solution, and very carefully titrated with semi-normal alcoholic potash added from a burette until the liquid is coloured faintly pink. The exact volume of potash solution used having been read off and recorded, about twice as much more is run into the flask from the burette, and the flask is then corked and boiled under an inverted condenser for 1 hour *; the excess of potash is then estimated by titration with semi-normal hydrochloric acid exactly as in determining the saponification value. The potash solution is standardized with the same acid.

On the first neutralization with potash in the cold, the following reaction takes place:—

$$\underset{\text{Acetyl-ricinoleic acid}}{C_{17}H_{32}(O.C_2H_3O)COOH} + KOH = \underset{\text{Potassium acetyl-ricinoleate}}{C_{17}H_{32}(O.C_2H_3O)COOK} + H_2O$$

The percentage of potash required for this reaction was called by Benedikt the *Acetyl Acid Value.*

By adding more potash and heating, saponification occurs, thus:—

$$\underset{\text{Potassium acetyl-ricinoleate}}{C_{17}H_{32}(OC_2H_3O)COOK} + KOH = \underset{\text{Potassium ricinoleate}}{C_{17}H_{32}(OH)COOK} + \underset{\text{Potassium acetate}}{KC_2H_3O_2}$$

the percentage of potash required for this reaction is called the *Acetyl Value.*

EXAMPLE.

2·5 grms. of the acetylated fatty acids from a sample of castor oil required 13·22 c.c. N/2 KOH for neutralization. 13·22 × 0·02807 = 0·3711 grm. KOH required for 2·5 grms. = 14·84 grms. KOH for 100 grms.; therefore the *Acetyl Acid Value* was 14·84.

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* A large excess of potash and long heating are necessary for the complete saponification of the acetylated acids.

26·22 c.c. more N/2 KOH were added, and after boiling for 1 hour 13·41 c.c. of N/2 HCl were required for neutralization. Therefore, the acetic acid formed on saponification required 26·22 − 13·41 = 12·81 c.c. N/2 KOH for neutralization, = 12·81 × ·02807 = 0·3598 grm. KOH for 2·5 grms. = 14·39 grms. KOH for 100 grms.; therefore the *Acetyl Value* was 14·39.

The results in the following table were obtained by Benedikt and Ulzer:—

TABLE LXV.—ACETYL VALUES OF OILS (*Benedikt*).

Description of Oil.	Mixed Fatty Acids.	Acetylated Acids.	
	Acid Value (KOH required for neutralization), per cent.	Acetyl Acid Value, per cent.	Acetyl Value, per cent.
Arachis (earthnut),	19·88	19·33	0·34
Olive,	19·71	19·73	0·47
Rape,	18·25	17·85	0·63
Peach-kernel,	20·25	19·60	0·64
Hempseed,	19·94	19·68	0·75
Walnut,	20·48	19·80	0·76
Croton,	20·10	19·57	0·85
Linseed,	20·13	19·66	0·85
Sesamé,	20·04	19·20	1·15
Poppyseed,	20·06	19·41	1·31
Cottonseed,	19·98	19·57	1·66
Grape seed (*Horn*),	...	...	14·45
Castor,	17·74	14·28	15·34
'Blown oil,'	...	18·45	6·22

Thus castor oil is sharply distinguished from the other natural oils (except grape-seed oil) by its high acetyl value, less sharply from blown oil, though 10 per cent. of the above sample of blown oil would lower the acetyl value of castor oil from 15·34 to 14·43 per cent.

It appears, however, that Benedikt's method of determining the acetyl values of oils is subject to an important error, which affects the above results in an, at present, unknown degree. Lewkowitsch * has found that pure stearic, oleic, and other fatty acids which contain no alcoholic hydroxyl may nevertheless give considerable acetyl values when treated by Benedikt's process. This he explains by stating that the fatty *acids* when boiled with a large excess of acetic anhydride are converted more or less completely into *anhydrides*, as shewn by the following equation:—

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* *Proc. Chem. Soc.* (1890), pp. 72, 91; *Jour. Soc. Chem. Ind.*, xix. (1890), p. 660.

$$\begin{array}{ccccccc} 2C_{15}H_{31}COOH & + & (C_2H_3O)_2O & = & (C_{15}H_{31}CO)_2O & + & 2CH_3COOH \\ \text{Palmitic acid} & & \text{Acetic anhydride} & & \text{Palmitic anhydride} & & \text{Acetic acid} \end{array}$$

When the acetylated product is boiled with water, the greater part of the anhydride is reconverted into acid,

$$(C_{15}H_{31}CO)_2O + H_2O = 2C_{15}H_{31}COOH,$$

but a variable proportion remains unchanged, and does not combine with potash *in the cold*; thus the acetyl acid value is too low. On *boiling* with potash, however, the anhydride readily undergoes hydrolysis, and, by neutralizing potash, causes a fictitious acetyl value to be obtained. This may account for the fact that the acetyl values obtained by other observers have not always agreed with Benedikt's numbers. Thus Wilson * gives the following average values for castor, olive, and cottonseed oils:—

Description of Oil.	Acetyl Acid Value, per cent.	Acetyl Value, per cent.
Cottonseed oil, ...	18·95	2·10
Olive oil, ...	17·00	3·60
Castor oil, ...	13·67	15·50

In order to avoid the error due to the formation of fatty anhydrides, Lewkowitsch at first proposed to determine the acetyl value by distilling off and estimating in the distillate the acetic acid formed by saponification of the acetylated fatty acids. He has since proposed to acetylate the glycerides themselves.

Lewkowitsch's Method.—10–20 grms. of the oil or fat, from which free fatty acids, if exceeding 5 per cent. in amount, should be first removed as directed on p. 208 (III.), or p. 209 (V.), are boiled for 2 hours with an equal volume of acetic anhydride and then washed by boiling with three successive half-litres of water for half-an-hour each time, as in washing the acetylated fatty acids in Benedikt's process (p. 236). The acetylated glycerides are further washed on a wet filter until every trace of acid is removed, and finally dried in the water-oven.

2-5 grms. of the acetylated oil are saponified by boiling for half-an-hour, under a reflux condenser, with 35 c.c. of semi-normal alcoholic potash, the soap solution is then rinsed with neutral alcohol into a porcelain basin and evaporated over the steam-bath until the alcohol is expelled. Absorption of CO_2 during this process need not be specially guarded against. The soap is dissolved in boiling water, rinsed into a 12-oz. flask, and decomposed by adding exactly the volume (ascertained by a separate experiment) of semi-normal hydrochloric acid or sulphuric acid necessary to neutralize the 35 c.c. of standard potash. The flask is closed by a cork carrying a long glass tube. The fatty acids will melt and form a clear oily layer on the surface of the liquid, and the acetic acid, together with any soluble fatty acid present, will dissolve in the aqueous liquid. When cold, the aqueous liquid is poured through a wet filter, and the fatty acids are thoroughly washed with hot, well-boiled distilled water free from CO_2 until the soluble acid is removed. This part of the process resembles the determination of the Hehner value (p. 226). The filtrate, which must be perfectly bright, is then titrated with decinormal alkali, using phenolphthalein as indicator, and, from the result, the number of grms. of potash required to neutralize the acetic acid formed on saponifying 100 grms. of the acetylated oil is calculated; this number is the *Acetyl Value* (*Lewkowitsch*), *per cent.*

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* *Jour. Soc. Chem. Ind.*, xi. (1892), p. 496.

The following numbers have been recorded by Lewkowitsch:—

TABLE LXVI.—ACETYL VALUES OF OILS (*Lewkowitsch*).

Description of Acetylated Oil.	Acetyl Value, per cent.
Olive oil,	1·35– 1·36
Rape oil,	0·79
Castor oil,	14·70–15·0
Cottonseed oil,	2·11– 2·51
Curcas oil,	0·84– 0·98
Maize oil,	0·79– 0·82
Linseed oil,	0·69
Animal oil,	2·24
Horse foot oil,	1·44
Tallow,	0·98
Shark liver oil,	1·78

Lewkowitsch acetyl values include the potash required to neutralize any soluble fatty acids present, as well as the acetic acid formed by the saponification of acetylated alcohols, including cholesterol and phytosterol, contained in a free state in the original oil. For this reason Lewkowitsch values are, as a rule, somewhat higher than Benedikt values.

B. Wachtel* has pointed out that oils and fatty acids which have undergone oxidation necessarily give greater acetyl values than the unoxidized substances. Samples of commercial stearic and oleic acids which he tested by Benedikt's process were found to have acetyl values of 0·0 and 6·2 per cent. respectively, which results he considers, as the oleic acid had probably undergone some oxidation, shew that Benedikt's method is capable of giving correct numbers. A sample of beef tallow, 15 years old, had an acetyl value of 5·37 per cent., doubtless owing to the presence of hydroxy acids formed by oxidation. These considerations and results shew the necessity of taking precautions to prevent oxidation of the fatty acids in preparing them for acetylation. They should be dried in a current of carbon dioxide. Any error due to oxidation of an oil or fat would obviously affect the acetyl value similarly, by whichever process determined.

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* *Jour. Soc. Chem. Ind.*, ix. (1890), p. 979.

Archbutt has made some experiments with blown oils.* These oils, when acetylated and boiled with water, emulsify and are troublesome to wash. It is necessary to boil with six successive quantities of water, each time for half-an-hour, otherwise the results are too high, and duplicate experiments do not agree. The acetylated *fatty acids* do not emulsify, and are much more easily washed. For this reason, the method first proposed by Lewkowitsch—viz., to acetylate the fatty acids and distil off the acetic acid formed—has advantages in such a case. But Benedikt's method gives quite satisfactory results. The following values were obtained with the same samples of oil by the two processes. In Benedikt's process the insoluble fatty acids were washed quite free from soluble acids before acetylation.

Description of Oil.	Acetyl Value of the Insoluble Fatty Acids by Benedikt's Process. Per cent.	Acetyl Value of the Glycerides by Lewkowitsch's Process. Per cent.
Castor oil, ...	14·95	15·02
„ (another sample), .	15·08	15·07
Blown East India rape oil, .	5·68	8·09
Blown ravison oil, . . .	5·37	7·97
Blown cottonseed oil, . .	6·96	9·83

Thus, castor oil gives practically the same result by both processes. Blown oils give a much lower result, and are therefore more sharply differentiated from castor oil, by Benedikt's process.

L.—THE IODINE VALUE.

1. Meaning and Use of this Value.

The iodine or Hübl value of a substance is the percentage of iodine absorbed from solution under definite conditions prescribed by Hübl in 1884.* The value of the test depends upon the fact that oils, fats and allied bodies are mixtures, in very variable proportions, of saturated and unsaturated compounds, and that whilst the latter readily unite with the halogens and form addition products the former do not. By bringing the oil and the halogen together in solution under conditions which reduce substitution to a minimum, it is found that the amount of halogen absorbed by each kind of fat and oil is very characteristic and affords one of the most reliable means we possess of distinguishing one kind of oil from another and of determining their proportion in mixtures.

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* Unpublished results. * Jour. Soc. Chem. Ind., iii. (1884), p. 641.

The test is most generally useful in the analysis of fixed oils and fats, but it has a limited value in the identification of mineral lubricating oil, vaseline, and paraffin wax. The halogen at first used was bromine. Allen published details of a bromine process in 1881,[*] and an improved process was described by Mills in 1883 and 1884;[†] but Hübl's iodine process has gradually superseded these. The use of bromine has recently been revived by Hehner in the form of a thermal test (see p. 247).

II. Determination of the Iodine Value.

(*a*) Hübl's Process.—The following solutions are required:—

Iodine Solution.—This is a solution, in ethyl alcohol, of iodine and mercuric chloride, in the proportion of at least one molecule of mercuric chloride to every molecule of iodine. The presence of mercuric chloride renders the absorption of the halogen by the fat more rapid and complete, and is essential for the attainment of constant results.[‡]

In preparing the solution according to Hübl's directions, 1 litre of pure 95 per cent. alcohol is divided into two equal parts; in one, 25 grms. of iodine are dissolved (heating hastens solution), and in the other, 30 grms. of powdered mercuric chloride (easily soluble in the cold); the two solutions are then mixed. The solution must be kept in a well-stoppered bottle in a dark, cool cupboard. At first the strength is about one-fifth normal, but the free iodine gradually and continually diminishes, at first rapidly and afterwards more slowly.[§] The solution, when freshly prepared, should be allowed to stand for from 6 to 12 hours before use. Every time it is used it must be standardized. Owing to the continual diminution of strength, a solution many weeks old can no longer be relied upon to give the maximum iodine absorption with substances of high iodine value, and, as the action of the iodine on the alcohol is much less rapid in the absence of mercuric chloride, it is far better to keep the solutions of iodine and mercuric chloride in separate bottles and to mix them only a few hours before being required for use.

Decinormal Thiosulphate Solution.—This may be prepared by dissolving 12·4125 grms. of pure, dry sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$) in water and diluting to 500 c.c. at 60° F. The re-crystallized salt, as purchased, is almost chemically pure, but generally damp; the crystals merely require crushing, drying by moderate pressure between folds of blotting paper and preserving in a well-stoppered bottle. If the above stated quantity of the dried salt be made up to exactly 500 c.c., the solution will be so nearly correct that for ordinary work it is not necessary to standardize it; and, if kept in the dark, it alters in strength very slowly. But it is easier and more satisfactory to prepare an approximately decinormal solution, by dissolving 12·5 grms. of the undried crystals, and to standardize this by means of pure potassium bichromate.

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[*] *Analyst*, vi. (1881), pp. 177 and 215.

[†] *Jour. Soc. Chem. Ind.*, ii. (1883), p. 435; iii. (1884), p. 366.

[‡] According to Wijs (*Analyst*, xxiii. (1898), p. 240) iodine monochloride is first formed, $HgCl_2 + 4I = HgI_2 + 2ICl$, and this reacts with the water of the alcohol to form hypoiodous acid, which is the active agent, thus:—$ICl + H_2O = HCl + HIO$.

[§] Owing, according to Wijs, to the fact that the hypoiodous acid gradually oxidizes the alcohol to aldehyde, thus:—$C_2H_6O + 2HIO = C_2H_4O + 2H_2O + I_2$. In this reaction, 2HIO (2 molecules) liberate I_2, whereas one molecule of undecomposed HIO liberates I_2 in the titration, thus:—$HCl + HIO + KI = KCl + H_2O + I_2$.

The pure bichromate is prepared by re-crystallizing the commercial salt a few times, and is obtained in the form of fine granular crystals by stirring and rapidly cooling a hot saturated solution. The crystals are filtered by suction, dried in the air-oven at 150°-200° C., and kept in a stoppered bottle.

For standardizing the thiosulphate, an accurate 1 per cent. solution of the bichromate is prepared, and is kept in a well-stoppered bottle. 10 c.c. of this solution are measured into an 8 oz. stoppered bottle and diluted with about 4 oz. of cold distilled water. 20 c.c. of a 10 per cent. solution of pure potassium iodide (free from iodate) are added, and about 10 c.c. of dilute sulphuric acid (1 part of strong acid to 3 parts of water). This acid liberates exactly 0·2584 grm. iodine, equivalent to about 20·4 c.c. of decinormal thiosulphate. The thiosulphate solution is then added from a burette, *in drops*,* with continual agitation of the liquid, until the colour of the free iodine has nearly disappeared. Starch solution is then added, and the titration is finished very slowly, by adding the thiosulphate at first two drops and then one drop at a time and allowing plenty of time between each addition, as the final destruction of the blue iodide of starch takes place slowly and it is easy to overshoot the mark. The colour of the solution is not bleached, but changes to the pale bluish-green of chromium chloride. If x be the number of c.c. used, then 1 c.c. of thiosulphate solution is equivalent to $\frac{0·2584}{x}$ grm. of iodine.

Potassium Iodide Solution.—This is a 10 per cent. aqueous solution of the pure salt free from iodate. It becomes slightly yellow on keeping, owing to liberation of iodine, but may be bleached by adding a drop or two of thiosulphate.

Starch Solution.—About 1 grm. of pure arrowroot starch is rubbed to a smooth cream with a few drops of water and poured into an 8 oz. conical beaker. The beaker is nearly filled with boiling water, immediately placed over the naked flame of an Argand-Bunsen for a few moments and allowed to boil up. It is then covered and left to stand over night, and the clear liquid is decanted for use. If required for use immediately, the hot liquid may be filtered.

Methylated Chloroform.—This must be proved to absorb no iodine. Place 10 c.c. and 20 c.c. in two stoppered bottles. Add to each, 10 c.c. of iodine solution, and stopper the bottles tightly, after moistening each stopper with a drop of potassium iodide solution. Place the bottles in a dark cupboard for several hours, and then titrate the free iodine in each; if the volume of thiosulphate used is the same for both, the chloroform is fit for use.

To determine the iodine value, as much of the substance is weighed in a very small counterpoised beaker as will absorb about 0·3 grm. of iodine, or a trifle more. It is dissolved in chloroform † and rinsed into a dry 8 oz. stoppered bottle, about 10 c.c. of chloroform being used altogether. About the same volume of chloroform is then poured into another similar bottle. Both bottles must have very well fitted stoppers.

The approximate strength of the iodine solution having been ascertained by titrating 10 c.c. with the standard thiosulphate, as much is measured into each bottle as will contain at least 0·6 grm. of iodine. If, after mixing, the contents of the bottle containing the substance be not clear, more chloroform is added, the same extra volume being added to the blank quantity. The bottles are then tightly stoppered, each stopper being first moistened with a drop of strong potassium iodide solution to make a more effective seal, and are placed in a cool, dark cupboard for not less than 6, and not more than about 18, hours. It is convenient to commence the experiment late in the afternoon and titrate the first thing next morning.

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* If the thiosulphate be added more rapidly an excessive quantity is required.

† In testing a substance which is insoluble in chloroform but soluble in alcohol, either the substance is transferred to the bottle in a dry state, or it is dissolved in 10 c.c. of absolute alcohol and exactly the same volume of absolute alcohol is added to the blank quantity.

Before commencing to titrate, each bottle, in warm weather, is first cooled by running some cold water over it, so as to produce a slight reduction of pressure inside, and a few drops of potassium iodide solution are poured round the stopper, which, on opening the bottle, are drawn in, rinsing the neck and stopper. 20 c.c. of potassium iodide solution are then poured into the bottle, and cold distilled water is added until the bottle is about two-thirds full. Part of the iodine will now be in the aqueous liquid, and part in the chloroform solution which settles to the bottom. The standard thiosulphate solution is next run in, at first rapidly and afterwards more slowly, with constant agitation, until the free iodine has nearly all disappeared, and then the starch solution is added and the titration is finished drop by drop, vigorously shaking the closed bottle between each drop, until the blue colour is destroyed. The difference between the volumes of thiosulphate solution used for the blank quantity and for the sample is calculated to iodine, and, when divided by the weight of substance taken and multiplied by 100, gives the iodine value.

EXAMPLE.

It was required to determine the iodine value of a sample of olive oil. 10 c.c. of iodine solution, rather old, required 17·2 c.c. of decinormal thiosulphate solution, equivalent to 0·217 grm. iodine; therefore, a 30 c.c. pipetteful would contain about 0·65 grm. iodine. Now olive oil, when genuine, absorbs about 80 per cent. of iodine; therefore, weighed out 0·4 grm. In titrating, the volumes of thiosulphate solution used were,

For the blank quantity, . .	50·80 c.c.
For the test quantity, . .	24·30 c.c.
Difference, ...	26·50 c.c.

1 c.c. of the thiosulphate used was equivalent to 0·01261 grm. iodine; therefore, 26·50 c.c. were equivalent to 0·33416 grm. Therefore, 0·4 grm. of the oil absorbed 0·33416 grm. iodine, and 100 grms. would absorb 0·33416÷0·4×100=83·54, which is the iodine value of the sample.

For the attainment of uniformly reliable and concordant results by this process, about double as much iodine should be added as the substance can absorb. The iodine solution must not be too weak, otherwise the maximum iodine absorption is not obtained with oils of high iodine value. The digestion with iodine must not be continued for too short a time, nor unduly prolonged; standing over night (about 18 hours) is sufficient in all cases. Although these precautions are more necessary when dealing with substances of high than of low iodine value, it is desirable to adopt the same method of working in all cases.

The chemical reactions taking place in this process are not so simple as Hübl supposed. Although addition of iodine, or of chlorine and iodine, is the main reaction, a variable amount of substitution takes place, which, however, does not interfere with the practical value of the results. See papers by Schweitzer and Lungwitz,* Ephraim,† and Waller,‡ and the discussion of the subject by Lewkowitsch (*Analysis of Oils*, pp. 175–180); also a valuable paper by Wijs.§

(*b*) **Wijs's Process.**—Wijs considers that the hypoiodous acid which is present in the Hübl solution ‖ is the active agent in bringing about the addition of iodine which, in the case of oleic acid, may be represented by the following equations:—

$$(1)\ C_{18}H_{34}O_2+HIO=C_{18}H_{34}O_2IOH.$$
$$(2)\ C_{18}H_{34}O_2IOH+HCl=C_{18}H_{34}O_2ICl+H_2O.$$

He has proposed, therefore, to replace the Hübl reagent with a solution of hypoiodous acid, as a means of shortening the time required for a determination. The fact, however, that this acid so readily

TABLE LXVII.—IODINE VALUES DETERMINED BY HÜBL'S AND WIJS'S METHODS.

Description of Oil.	Excess of Iodine, per cent.	Time of Contact.	Iodine Value.
Linseed oil, . . .	68	4 hours	180·91 (*Hübl*)
„ . . .	57	5 minutes	181·58
„ . . .	57	7 „	182·25
„ . . .	57	10 „	182·17
Maize oil, . . .	68	4 hours	124·87 (*Hübl*)
„ . . .	65	3 minutes	127·55
„ . . .	64	6 „	128·56
„ . . .	64	7 „	128·38
Sesame oil, . . .	69	4 hours	110·35 (*Hübl*)
„ . . .	68	5 minutes	111·87
„ . . .	57	7 „	111·75
Cottonseed oil, . .	68	4 hours	108·76 (*Hübl*)
„ . . .	59	3 minutes	110·07
„ . . .	59	7 „	109·83
Rape oil, . . .	68	4 hours	102·96 (*Hübl*)
„ . . .	65	3 minutes	103·08
„ . . .	61	7 „	103·33
Earthnut oil, . . .	74	4 hours	87·26 (*Hübl*)
„ . . .	70	2 minutes	86·89
„ . . .	70	3 „	87·13
„ . . .	70	7 „	87·25
Olive oil, ...	70	4 hours	83·27 (*Hübl*)
„	70	3 minutes	84·39
„	70	7 „	84·45

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* *Jour. Soc. Chem. Ind.*, xiv. (1895), pp. 130 and 1030.

† *Analyst*, xx. (1895), p. 176.

Ibid., p. 280.

§ *Ibid.*, xxiii. (1898), p. 240.

‖ See footnote on p. 241.

ABLE LXVIII.—Hübl Iodine Values of Fixed Oils, Fats, and Waxes, and their Mixed Fatty Acids.

Class.	Name of Oil, etc.	*Iodine Values.* Iodine Absorbed by 100 Parts	
		Of Oil, Fat, etc.	Of Mixed Fatty Acids.
egetable n-drying s and fats.	Olive oil,	76 –89 (rarely exceeds 85)	86 – 90
	Olive kernel oil,	87 – 88	..
	Arachis (earthnut) oil,	84·5–105	95·5–103·5
	Castor oil,	83·5– 86·5	86·5– 88·5
	Palm oil,	51 – 52·5	53·5
	Palm nut oil,	10 – 17·5	12
	Coconut oil,	8 – 9·5	8·5– 9·5
	Japan wax,	4 – 7	..
	Cottonseed stearin,	88·5–104	94·5
egetable ni-drying oils.	Rape oil,	97·5–106	96·5–105·5
	Ravison oil,	110 –122	126
	Mustard oil (black),	96 –106·5	109·5
	Mustard oil (white),	92 – 98·5	94·5– 96
	Cottonseed oil,	101 –117	111 –115·5
	Curcas oil,	98 – 99	..
	Sesamé oil,	102·5–112	109 –112
	Beech nut oil,	104 –111	114
	Brazil nut oil,	106	108
	Maize oil,	111 –123	113 –125
	Cameline oil,	132·5–135·5	137
egetable ying oils.	Linseed oil,	170 –195·5	155 –182
	Hempseed oil,	140·5–157·5	122 –141
	Nigerseed oil,	133 –133·5	147·5
	Poppyseed oil,	132·5–143·5	116·5–139
	Sunflower oil,	120 –135	124 –134
	Walnut oil,	132 –151·5	150
Animal and fats.	Lard oil,	67 – 82	..
	Neatsfoot oil,	..	62 – 63·5
	Tallow oil ('animal oil'),	60	..
	Tallow (beef, mutton, and home refined),	32·5– 50	26 – 41·5
	Bone fat,	46·5– 56	55·5– 57·5
	Horse fat,	71·5– 86	84 – 87
	Lard,	46 – 64	64
Marine mal oils and d waxes.	Sperm and bottlenose oils,	76·5– 84	82 – 88
	Porpoise body oil,	77	..
	Porpoise jaw oil, strained from solid fat,	31 – 50	..
	Porpoise jaw oil, unstrained,	77	..
	Dolphin body oil,	99·5	..
	Dolphin jaw oil, strained from solid fat,	33	..
	Whale oil,	120 –130	130 –132
	Seal oil,	125 –152·5	..
	Menhaden oil,	148 –160	..
	Sardine oil, Japanese,	96 –121·5	..
	Shark liver oil,	90 –114·5	..
	Cod liver oil,	123 –168·5	130·5–170
	Haddock and skate liver oils,	154 –157·5	..
Waxes (solid).	Wool fat,	26 – 29	17 – 18
	Spermaceti (if free from sperm oil),	nil.	..
	Beeswax,	8 – 11	..
	Carnauba wax,	13·5	..

decomposes ($5HIO = HIO_3 + 2H_2O + 4I$) prevents it from being employed with any advantage at first hand. It was found best to obtain it by the action of water on iodine chloride ($ICl + H_2O = HCl + HIO$), using a solvent which contained only sufficient water to decompose nearly the whole of the iodine chloride, and which at the same time would not be oxidized by the hypoiodous acid when formed. Good results were obtained by using as the solvent 95 per cent. acetic acid.

TABLE LXIX.—HÜBL IODINE VALUES OF MISCELLANEOUS SUBSTANCES.

Class.	Description.	Iodine Value. = Iodine absorbed by 100 parts.
Blown oils.	Blown rape oil,	63·6 (1 sample)
	Blown cottonseed oil,	56·4 („)
Alcohols.	Alcohols from sperm oil,	59·5–69·3
	Alcohols from wool fat,	36·0–39·4
	Cholesterol and phytosterol,	67·3–68·1
Resins.	Colophony,	128·9
Solid hydrocarbons.	Paraffin wax,	3·9– 4·0
	Ozokerit,	4·5– 4·9
	Vaseline (Chesebrough Co.),	8·6
American lubricating oils.	Pale '885,'	12·52
	'Red' engine oil,	16·06
	Dark medium machinery oil,	14·15
	Dark cylinder oil,	15·62
Russian lubricating oil.	'Ragosine' oil No. 1,	7·19
Shale oil.	Scotch shale oil, '890,'	22·99
	Rosin oil,	43–48

The reagent is prepared by dissolving 13 grms. of iodine in 1 litre of the acid, determining the titre of the solution, and then passing into it a current of chlorine (free from hydrochloric acid) until the titre is doubled. With a little practice the exact point can be hit by observing the change in colour. The solution thus obtained is employed in precisely the same manner as Hübl's solution, except that the time required for the absorption is very greatly shortened. In the case of oils with low iodine values, absorption is said to be complete in from 3–4 minutes; with those of higher value not more than 10 minutes are necessary, if too much oil has not been used. Table LXVII. gives some of the results obtained by Wijs with his reagent as compared with Hübl's reagent.

In almost every case the numbers by Wijs's process are higher than the Hübl value, but the author of the process considers them the more correct by reason of the results obtained with purified allyl alcohol. This has a theoretical iodine value of 435. By Hübl's process, Lewkowitsch obtained values ranging from 349–376. Using 75 per cent. excess of iodine, Wijs obtained by Hübl's process an iodine value of 425, and by his own process he obtained values of 434·1 after 5 minutes' and 436·8 after 10 minutes' contact.

M.—HEHNER'S BROMINE THERMAL TEST.

Hehner and Mitchell have devised a very useful method for the rapid determination of iodine values indirectly. Hehner had shewn[*] that when liquid bromine is added to an oil or fat dissolved in chloroform or carbon tetrachloride, instantaneous combination occurs, accompanied by considerable evolution of heat, and in conjunction with Mitchell he subsequently discovered that the heat evolved, measured by the rise of temperature under fixed conditions, bears a nearly constant ratio to the iodine value; that, in fact, the iodine value, which by Hübl's process takes several hours to determine and involves the use of a special reagent not always ready, can be ascertained with considerable accuracy in a few minutes by measuring the thermometric rise with bromine and multiplying the result by a constant.

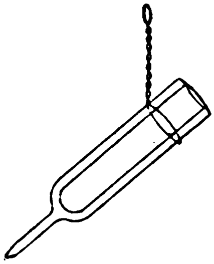

FIG. 70.—VACUUM JACKETED TUBE.

The following apparatus and reagents are required :—

A vacuum-jacketed tube,[†] measuring internally 3½ inches in length × ⅞ inch in diameter.

A Centigrade thermometer, divided in fifths of a degree from, say, 0° to 50°.

A 1 *c.c. pipette*, having a short soda-lime tube fixed by a cork to the upper end, with a flexible tube for mouthpiece.

Liquid bromine, and

Methylated chloroform.

The Process.—The vacuum-jacketed tube is suspended from the right hand arm of the balance by means of a stiff platinum wire loop (fig. 70), a

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[*] *Analyst*, xx. (1895), p. 49.

[†] Obtainable from Messrs. Baird and Tatlock.

> counterpoise made from a piece of thick sheet lead being placed in the other pan. By opening the side door of the balance case, the oil or fat can be dropped into the tube and the exact weight easily and quickly adjusted. The tube is then slipped out of the wire loop and fixed firmly, by means of the short stem, in a suitable stand, and 10 c.c. of chloroform are introduced by a pipette. The temperature of the bromine is next ascertained to the nearest 0·1 deg., by stirring with the thermometer, and the same thermometer, freed from adhering bromine, is then immersed in the chloroform solution of the substance, which is brought to exactly the same temperature as the bromine, either by warming the outer tube by the hand or cooling it by immersion in cold water. This adjustment takes place slowly, as the heat can only be transmitted by radiation. Immediately the temperature is correctly adjusted, 1 c.c. of the bromine is withdrawn from the bottle and added to the chloroform solution, which is rapidly stirred with the thermometer until the mercury has risen to the highest point and begun to fall again. As this takes place in about 15 seconds, close observation of the mercury is necessary. The difference between the initial and final temperatures is the rise of temperature.
>
> It is desirable to vary the quantity of substance taken, according to the amount of heat developed. Of olive and rape oils, 1 grm. is a suitable quantity; of tallow or any other fat composed mainly of saturated glycerides, 2 grms. may be used; but of linseed oil, which reacts very violently with bromine, 0·5 grm. is sufficient. 10 c.c. of chloroform and 1 c.c. of bromine are used in all cases. The rise of temperature when 2 grms. are used is divided by 2, and when 0·5 grm. is used is multiplied by 2. The result, expressed by the symbol β, may be called the *bromine thermal value.*

The numerical value of the constant or factor for converting the bromine thermal values into iodine values depends upon the heat capacity of the particular tube and thermometer used. Hehner and Mitchell found it to be about 5·5, Jenkins* 5·7, Archbutt† from 5·7 to 6·2, according to the nature of the oil. Each operator, in a test of this kind, must of necessity work out his own factors, by making comparative determinations of the Hübl iodine values and the bromine thermal values of about half a dozen genuine samples of each description of oil which he wishes to use the method for.

The results of consecutive experiments made with the same sample of oil are remarkably concordant, the extreme difference usually observed being 0·3° C. Duplicate experiments, made at intervals of several days, usually agree within 0·1° C. Bromine as purchased, the same fully saturated with water, and the same dehydrated by shaking with strong sulphuric acid and distilling, gave practically the same results, as the figures in Table LXX., obtained with the same sample of rape oil, shew.

The results of experiments with four descriptions of oil are given in Table LXXI., and it will be seen that the agreement between the observed and the calculated iodine values is generally very satisfactory. Thus, with the seven samples of tallow, the maximum difference is 1·7; in the case of the olive oils, it is 2·5; eleven samples of rape oil gave a maximum difference of 1·5; and the agreement in the case of raw linseed oil is nearly as good. The

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* *Jour. Soc. Chem. Ind.*, xvi. (1897), p. 193.

† *Ibid.*, p. 309.

TABLE LXX.

EXPT.	THERMAL VALUE (β). °C.		
	Bromine as Purchased.	Bromine saturated with Water.	Anhydrous Bromine.
1	20·4	20·2	20·1
2	20·3	20·4	20·2
3	20·1	...	...
4	20·2	...	...
Mean,	20·25	20·3	20·15

TABLE LXXI.

1. **TALLOW.** 7 samples (2 grms. used; the rise of temperature ÷ 2 = β).

Description.	Bromine Thermal Value (β).	β × 6·2.	Hübl Iodine Value.
American beef, . .	6·1	37·8	39·1
Home refined, . .	6·7	41·5	41·3
,, . .	6·7	41·5	41·8
,, . .	7·05	43·7	44·3
,, . .	7·2	44·6	44·9
Australian mutton, .	7·55	46·8	46·3
Home refined, . .	8·9	55·2	53·5

2. **OLIVE OIL.** 10 samples (1 grm. used; the rise of temperature = β).

Description	Bromine Thermal Value (β).	β × 5·7.	Hübl Iodine Value.
Unknown, . . .	13·55	77·2	78·7
,, . . .	13·8	78·7	78·9
Malaga, ...	13·8	78·7	79·3
,, ...	14·2	80·9	78·4
Unknown, . . .	14·2	80·9	81·4
,, . . .	14·35	81·8	81·4
Gallipoli, . . .	14·4	82·1	82·0
Unknown, . . .	14·45	82·4	84·2
Gallipoli, . . .	14·5	82·6	82·5
,, . . .	14·5	82·6	82·1

3. **RAPE OIL.** 11 samples (1 grm. used; the rise of temperature = β).

Description.	Bromine Thermal Value (β).	β × 5·92.	Hübl Iodine Value.
Stettin, ...	17·0	100·6	99·6
Unknown, . . .	17·35	102·7	102·7
,, . . .	17·4	103·0	103·3
,, . . .	17·3	102·4	103·1
,, . . .	17·7	104·8	105·7
,, . . .	17·8	105·4	104·6
,, . . .	17·9	105·9	106·2
,, . . .	18·25	108·0	108·1
,, . . .	18·6	110·1	109·4
Black Sea, . . .	19·1	113·1	113·5
,, . . .	20·3	120·2	121·7

4. **RAW LINSEED OIL.** 10 samples (0·5 grm. used; the rise of temperature × 2 = β).

Description.	Bromine Thermal Value (β).	β × 6·0.	Hübl Iodine Value.
Old sample, . .	28·5	171·0	167·1
Unknown, . . .	28·8	172·8	177·0
American (?), . .	29·6	177·6	177·0
Unknown, . . .	29·7	178·2	177·8
Calcutta, . . .	29·8	178·8	178·7
,, . . .	30·45	182·7	183·3
Baltic, ...	31·35	188·1	188·5
,, ...	31·4	188·4	188·8
,, ...	31·75	190·5	188·8
,, ...	32·5	195·0	192·5

greatest difference observed in testing ten samples of the latter oil was [illegible], but if we omit the first two samples the difference does not exceed [illegible]. These results prove that the bromine thermal test is a valuable auxiliary method for the valuation of oils, which, in laboratories where a large number of oils of the same kind have to be examined, may save a great deal of time and labour.

V.—MAUMENÉ'S THERMAL TEST.

All the fixed oils react with strong sulphuric acid with evolution of heat, which is least in the case of the non-drying and greatest in that of the drying oils. In Maumené's test, 50 grms. of the oil are mixed in a beaker with 10 c.c. of strong sulphuric acid, both at the same initial temperature, and the rise of temperature is read off. This varies from about 4[illegible]° C. with olive oil to about 130° C. with linseed oil, and as the limits of variation with different pure samples of each oil are not wide, the test, when conducted with due care, is a valuable means of distinguishing one oil from another and of detecting adulteration.

The attainment of uniform results by this test depends upon the employment of constant conditions, especially as regards the strength of the sulphuric acid used. The following results by Archbutt* show the effect of varying the strength of the acid, all other conditions remaining the same.

TABLE LXX[illegible].

Description of Oil.	Rise of Temperature (° C.) with Acid containing per cent. of H_2SO_4						
	[illegible]	[illegible]	[illegible]	94·72	93·75	92·73	91·85
[illegible]	[illegible]	[illegible]	[illegible]	3[illegible]·5	34·5	31	28·6
[illegible]	[illegible]	4[illegible]·3	44	40·5	38·7	35·5	32·5
[illegible]	[illegible]	[illegible]	58	54	50·3	47	41·7

As the temperature rises more slowly the weaker the acid, it is advisable to use acid containing not less than 97 per cent. of H_2SO_4, and its strength must be ascertained by analysis, since the specific gravity of sulphuric acid reaches the maximum at 97·7 per cent., and then diminishes, so that acids of 95·6 per cent. and 99·2 per cent. strength have the same specific gravity (*Lunge and Naef*).

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* Jour. Soc. Chem. *Ind.*, v. (1886), p. 303.

he method of working which we recommend, involves the use of ıe following reagent and apparatus:—

Sulphuric Acid (97% H_2SO_4); prepared as follows:—The contents of an nopened Winchester quart bottle of pure sulphuric acid are well mixed, bout 6 c.c. are then taken out with a dry pipette, quickly delivered into a ry weighing bottle, which is stoppered and the exact weight taken. The :id is then carefully diluted with cold water, made up to exactly 500 c.c. at ıe temperature of the laboratory and well mixed. 100 c.c. of the diluted :id are next measured with a pipette and delivered into a 16-oz. flask, conıining a weighed quantity of pure sodium carbonate dissolved in a small uantity of water. 1·10 grms. of sodium carbonate are taken for every 1 grm. f acid. This weight of the nominally dry carbonate is placed in a tared latinum crucible, gently ignited over a spirit flame for 10 minutes, cooled ı the desiccator with a cover on the crucible, and the exact weight then ıken. After the acid has been run into the sodium carbonate solution, the quid is heated to boiling to expel most of the carbonic acid, then made uite cold, and the excess of sodium carbonate estimated by titration with ecinormal acid, using methyl orange as indicator. In order that the end oint of the titration may be sharply observed, the colour of the liquid should e compared with that of an equal volume of pure water tinted with the ıme quantity of methyl orange and contained in an exactly similar flask. 'he following is an example of the calculation:—

		Grms.
Weight of sulphuric acid titrated = $\frac{1}{5} \times 11·1110$	=	2·2222
Weight of dry Na_2CO_3 taken,	=	2·4493
N/10 acid, 13·38 c.c. = Na_2CO_3 13·38 × ·0053	=	·0710
Weight of dry Na_2CO_3 neutralized,	=	2·3783
Equivalent weight of H_2SO_4	=	2·1980
∴ *Strength of Acid* = 2·1980 ÷ 2·2222 × 100	=	98·98% H_2SO_4

If the acid be weaker than 97 per cent., it is rejected: if stronger, it is iluted to exactly 97 per cent. strength by adding to a weighed quantity, say kilo, the requisite quantity of pure water, which may be measured from a elicate burette and well stirred into the acid. The reagent thus prepared ı preserved for use in a capped ether bottle; the stock is kept in the Winchester,' the stopper of which, after wiping free from acid, is smeared rith a little vaseline and tied down.

Beakers, tall form, 4 inches high by 2½ inches in diameter. These fit into nest of cotton-wool contained in a 40-oz. lipped beaker.

A 10 c.c. burette, with glass tap. The orifice of the jet is reduced by holding ; in the Bunsen flame until, with the tap turned full on, 10 c.c. of the ılphuric acid take one minute, within a second or two, to flow out.

A Centigrade thermometer, graduated in single degrees from 0° to 100°.

In making a test, the temperature of the air of the room is first of all ascerıined, and the acid is then brought to the same temperature by warming the ottle by the hand or by cooling it in water. Exactly 50 grms. of the oil, aving been weighed into the beaker, are stirred with the thermometer and rought to the same temperature as the acid, and the beaker is then placed ı the cotton-wool nest. The burette having been filled with the acid and overed by a glass cap, the beaker is brought under it, the tap is opened wide, nd 10 c.c. of acid are allowed to run into the oil, all the time stirring the oil nd the acid most thoroughly together. After the acid is all in, the stirring is continued until the mercury ceases to rise. The [illegible] is read off, the initial temperature is deducted, and the difference is the rise in the temperature.

When a number of samples are being tested, a thermometer is kept suspended near the burette to record the temperature of the acid, and if this alters, the initial temperature of the oil must be altered accordingly. Immediately after testing each oil the burette is refilled with acid and stoppered, and the neck of the bottle is carefully wiped dry and capped. If these directions are followed, very good results may, with practice, be obtained.

This test is most useful in comparing one sample of oil with another, as in controlling the quality of the deliveries of oil [illegible] to sample. As the results obtained are influenced not only by the strength of the acid used but also by the exact method employed, each observer must construct a table of results for himself by testing several pure samples of each oil he requires to examine. The following table will serve to shew, approximately, the results obtained with some well-known oils:—

TABLE LXXIII.

Name of Oil.	Rise of Temperature with [illegible] Degrees Centigrade.
Animal oil,	[illegible]
Olive oil,	[illegible]
Arachis oil,	[illegible]
Castor oil,	[illegible]
Rape oil,	[illegible]
Sesamé oil,	[illegible]
Ravison oil,	[illegible]
Cottonseed oil,	[illegible]
Poppyseed oil,	[illegible]
Nigerseed oil,	[illegible]
Seal oil,	[illegible]
Menhaden oil,	[illegible]
Linseed oil,	[illegible]

In testing oils which evolve more heat than cottonseed oil the thermal [illegible] so violent that the liquid froths out of the beaker; therefore the test cannot be made unless the oil is diluted. For this purpose [illegible] 20 grms. of linseed oil diluted with 30 grms. of olive oil give a moderate thermal effect. The olive oil must be tested separately to ascertain the rise of temperature obtained with it alone, the thermal rise of the linseed oil is then calculated as shewn by the following example:—

Rise of temperature of the mixture, observed,	77·2°
Effect due to 30 grms. of olive oil $= \frac{3}{5} \times 42° =$	25·2°
Effect due to 20 grms. of linseed oil,	52·0°
∴ 50 grms. of linseed oil would rise $\frac{5}{2} \times 52° =$	130°

Specific Temperature Reaction.—Thomson and Ballantyne * have proposed to avoid the trouble involved in the preparation of an acid of known strength by a new method of recording results. Instead of stating the rise of temperature in degrees, they propose to express the result in terms of the rise of temperature with water at 20° C. taken as 100.

Exactly 50 c.c. (=50 grms.) of water are delivered into the beaker from a pipette, brought to 20° C., and mixed with 10 c.c. of sulphuric acid also at 20° C. The acid is run into the water exactly in the same way and at the same rate as into an oil, but the experiment is not so easy, as in stirring the water and acid together in the absence of a lubricant, one is very apt to crack the beaker, and the temperature with water does not remain for some time stationary at the maximum, as with oil, but quickly begins to fall. Having, however, successfully made the experiment, preferably in duplicate, the oil is tested in the same way and in the same beaker. The result with oil is then divided by the mean result with water, and the quotient, multiplied by 100, is the '*Specific Temperature Reaction.*' The following table by Thomson and Ballantyne shews the results they obtained by operating in this way with acids of three different strengths:—

TABLE LXXIV.

Sample.	H_2SO_4 95·4 %.		H_2SO_4 96·8 %.		H_2SO_4 99·0 %.	
	Rise of Temperature °C.	Specific Temperature Reaction.	Rise of Temperature °C.	Specific Temperature Reaction.	Rise of Temperature °C.	Specific Temperature Reaction.
Water, . . .	38·6	100	41·4	100	46·5	100
Olive oil, . .	36·5	95	39·4	95	44·8	96
	...	...	39·0	94	43·8	94
	34·0	88	38·1	92	44·2	95
Rape oil, . .	49·0	127	...	...	58·0	124
Castor oil, . .	34·0	88	37·0	89	...	...
Linseed oil, . .	104·5	270	...	...	125·2	269

Thomson and Ballantyne found, when testing the same sample of olive oil in two different beakers, one 3 inches and the other 4 inches in height, but both 2 inches in diameter, that the temperature rose 2 deg. higher in the taller beaker; the same difference was observed with water; therefore, in whichever beaker the experiments were made, the specific temperature reaction, calculated from the thermal effects with water and oil in the same beaker, were almost identical, the figures being 93·5 and 93·8.

The evolution of heat on mixing oils with sulphuric acid proceeds from a variety of chemical reactions, *e.g.*, saponification or hydrolysis of the glycerides, sulphonation of the fatty acids and glycerin, and, as the temperature rises, destructive oxidation accompanied by charring and evolution of sulphur dioxide. The evolution of heat depends largely upon the proportion and nature of the unsaturated fatty acids present, and bears a more or less definite relation to the iodine value. The relation, however, according to Hehner and Mitchell, is quite different with different oils and fats, unlike the relation between the bromine thermal value and the iodine value, which is nearly the same for most oils and fats. The following comparative results obtained by Archbutt with rape oil shew that, although the iodine value may be calculated very nearly from the Maumené figure, the bromine thermal value is a more reliable basis for calculation, notwithstanding the fact that the multiplier in the latter case is more than three times as large as in the former.

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* *Jour. Soc. Chem. Ind.*, x. (1891), p. 233.

TABLE LXXV.

Sample of Rape Oil.	Iodine Value by Hübl's Process.	Iodine Value Calculated from the Bromine Thermal Value. [illegible] × 5·5.	Iodine Value Calculated from the Sulphuric Acid Thermal Value. [illegible] × 1·6.
No. 1	102·7	102·7	99·4
„ 2	103·3	103·0	101·4
„ 3	103·1	102·4	101·9
„ 4	105·7	104·5	106·5
„ 5	104·6	105·4	104·3
„ 6	106·2	105·5	106·0
„ 7	106·1	[illegible]	109·9
„ 8	109·4	110·1	111·4

Q.—OXIDATION AND GUMMING OF LUBRICATING OILS.

I. Fixed Oils.—No absolute quantitative method of determining the oxidizing properties of lubricating oils is known. The behaviour of the different fixed oils when exposed in thin films to the air at the ordinary or a slightly elevated temperature, leads to their classification in three divisions, viz.:—(1) *drying oils*, which by oxidation soon solidify to a varnish and therefore include the paint oils; (2) so-called *non-drying oils*,* which remain fluid for long periods and comprise the best lubricating oils; and (3) *semi-drying oils*, which form an intermediate class, drying but slowly, yet too oxidizable to be well adapted for lubricating. Rape oil, however, which is the least oxidizable of the semi-drying oils, is largely used as a lubricant by large consumers, owing to its comparatively low cost.

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* Livache has shewn (*Jour. Soc. Chem. Ind.*, xiv. (1895), p. 811) that all fixed oils, whether vegetable or animal, and even fats, if exposed to the air at a sufficiently high temperature (120°-160° C). sooner or later dry up, forming a solid elastic product similar to that obtained from the drying oils.

In the examination of olive oil, lard oil, sperm oil, and other well-known lubricating oils belonging to the non-drying class, also fats such as tallow, it is as a rule sufficient to prove the absence of adulterants belonging to the drying and semi-drying classes, by means of the ordinary physical and chemical tests, paying special attention to the iodine value, which is increased by the presence of the more easily oxidizable oils. But with rape oil the case is different. Genuine rape oils, or at any rate oils which the analyst is unable to certify as adulterated, differ considerably in gumming properties, and a special oxidation test is not only useful but practicable, as rape oil is sufficiently oxidizable to give a decided result in a reasonable time. The following simple comparative test is usually made:—

(*a*) **Watch-glass Test.**—1 grm. of the sample of oil is weighed on a watch-glass, the same weight of a standard sample is weighed on another watch-glass of the same curvature, and the two glasses are placed side by side in a boiling-water oven, where they are left undisturbed for a certain number of hours. A good practice is to place the glasses containing the oils in the oven at, say, 5 p.m. and take them out at 9 a.m., *i.e.*, after an interval of 16 hours. The condition of the oils is then examined when cold.

Tested in this way, and using 1 grm. of the substance, rape oil of the very best quality does not dry, and does not appear to have thickened much when caused to flow by inclining the glass; inferior samples will have crept up and formed dry spots on the sides of the glass, and most rape oils will have thickened more or less considerably. The result of this test, considered in conjunction with the physical and chemical data, is of considerable assistance in judging the quality of rape oil.

The same test is sometimes useful in the examination of olive oil. In this case 0·5 grm. should be used for the test, the other conditions remaining the same. Good olive oil will change very little in 16 hours, inferior oil, dark green or greenish-brown in colour, will thicken considerably.

The object of using a weighed quantity of oil is merely to ensure uniform conditions, equal weights of oil in glasses of the same curvature exposing the same surface area; it is not worth while to attempt to get more out of the test by weighing the oil after exposure, as the changes in weight due to oxidation are small and erratic, some of the products of oxidation being volatile at 100° C., they are also affected by variable traces of moisture in the oils, and no satisfactory result is thus obtained. (See Livache's test.)

(*b*) **Film Test.**—A less simple, but for some purposes a better test than the above, is made by exposing the oil in a film on a glass plate at a temperature of 50° C. It is not easy to obtain continuous films, nor films of uniform thickness, and unless they are uniform the results are not comparable. The least trace of moisture on the surface of the glass, even the film of moist air condensed on all apparently dry cold surfaces, causes some oils to draw up into irregular patches and drops. This may be avoided by first heating the glass strongly and painting it with the oil while still hot.

Pieces of plate glass, say 3 inches square and 3/16 inch thick, are carefully cleaned, wiped dry, and weighed. Each glass is numbered, and its approximate weight is marked on a card. The glasses are first heated in an air-oven to 200° C. for about ½-1 hour, then taken out and laid upon pieces of cork. As soon as they have cooled down to about 100°, the upper surface of each is thinly painted over, by means of a clean camel-hair brush, with the oil to be tested, and the glasses are then left to become quite cold. When cold they are placed again on the balance, and more oil is dropped upon the centre of each plate until exactly 0·1 grm. has been made up. The plates are then laid with the oiled sides upwards upon a levelled sheet of plate glass, in an oven furnished with a regulator, by which the temperature can be maintained at the temperature of 50° C. The oil last added will gradually spread over the surface of the glass. At intervals of a few hours the plates are removed from the oven, allowed to cool down to the temperature of the laboratory, and the condition of the oil tested by touching with the finger.

Even with the precaution above stated, the film will be thicker in some parts than others, and will not always dry at a uniform rate; but by making duplicate tests very fairly comparable results may be obtained. As a result of several tests made in this way it has been found that refined cottonseed oil dries to a varnish in from 18 to 24 hours, refined rape oil requires about 48 hours to dry to the same extent, whilst olive oil does not dry in 13 days.

The following results by Holde* were obtained by spreading '1 drop' of the oil on a glass plate measuring 5 × 10 centimetres and exposing to air at 50° C. for 24 hours. The film thus obtained would be thinner than that formed in the above described test, and might be expected to dry more quickly.

TABLE LXXVI.—EFFECT OF EXPOSING SOME FIXED OILS IN THIN FILMS TO AIR AT 50° C. (*Holde*).

Kind of Oil.	Consistence after 24 Hours' Exposure.	Kind of Oil.	Consistence after 24 Hours' Exposure.
Sperm oil, .	unchanged.	Mustard oil, . .	sticky, to dry.
Castor oil, . .	"	Earthnut oil, . .	"
Seal oil, . . .	"	Sesamé oil, . .	dry.
Olive oil, . . .	unchanged, or slightly thickened.	Cottonseed oil, .	"
		Sunflower oil, . .	"
Almond oil, . .	perceptibly thickened.	Poppy oil, . .	"
Crude rape oil,	perceptibly thickened. to sticky.	Fish oil, . . .	"
		Cod liver oil, . .	"
Refined rape oil, .	sticky, to dry.	Train oil, . . .	"
Whale oil,	thicker, to sticky.		

(c) Livache's Test. Increase of weight by oxidation.—Any attempt to measure the rate of oxidation of fixed oils by ascertaining the increase of weight at elevated temperatures is met by the difficulty that some of the products of oxidation are volatile. Thus Kissling * found, by passing air through linseed oil heated to 100° C., that of 0·87 per cent. of oxygen taken up daily 0·46 per cent. was carried away in the form of volatile acids of the methane series, carbon dioxide, and other products. Experiments by the same author on oils exposed to the air at 100°–105° C. in clock glasses shewed that the loss of weight by volatilization frequently exceeded the gain of weight by oxidation.† On the other hand, the gain of weight at the ordinary temperature is much too slow to be made the basis of a practical test.

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* *Die Untersuchung der Schmiermittel*, p. 98.

Livache, however, has shewn that the rate of oxidation is greatly accelerated by mixing the oil with finely-divided copper, tin or lead, the latter giving the best results.

The lead is prepared from solution of a lead salt by precipitation with sheet zinc, washing the precipitate well with water, alcohol, and ether, and drying in vacuo. About 1 grm. of the dry powder is spread out on a large tared watch-glass, and an accurately weighed quantity, somewhat over 0·5 grm. but not exceeding 0·7 grm., of the oil is spotted over it from a pipette, taking care that the drops do not run into one another. The whole is then weighed and allowed to remain exposed to light and air at the ordinary temperature.

Livache obtained the following results :—

TABLE LXXVII.—INCREASE OF WEIGHT OF OILS BY OXIDATION.

KIND OF OIL.	PERCENTAGE INCREASE OF WEIGHT.		
	Of Oil after		Of Fatty Acids after 8 Months.
	2 Days.	7 Days.	
Linseed oil, ...	14·3	...	11·0
Walnut oil, ...	7·9	...	6·0
Poppyseed oil, ...	6·8	...	3·7
Cottonseed oil, ...	5·9	...	0·8
Beech nut oil, ...	4·3	...	2·6
Colza oil, ...	nil.	2·9	2·6
Rape oil, ...	„	2·9	0·9
Sesamé oil, ...	„	2·4	2·0
Arachis oil, ...	„	1·8	1·3
Olive oil, ...	„	1·7	0·7

Drying oils tested in this manner commence to gain weight rapidly, the maximum increase taking place in a few days, whereas the non-drying oils must be left for fully seven days before any useful result is obtained. Evidently this test is unsuited for the

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* *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 479.

† Lewkowitsch, *Analysis of Oils, etc.*, p. 265.

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	−[illegible]	−[illegible]	−1·[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	1·[illegible]	[illegible]
[illegible]	[illegible]	1·[illegible]	2·[illegible]	[illegible]
[illegible]	[illegible]	4·20	3·[illegible]	3·[illegible]
72	[illegible]	...	4·50	...
96	5·[illegible]	5·60	5·00	[illegible]
[illegible]	...	5·[illegible]	...	5·10
[illegible]	6·40	...	5·80	...
[illegible]	...	6·40	...	5·90

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* *Jour. Soc. Chem. Ind.*, xv. (1896), p. 476.

TABLE LXXIX.—CHANGE OF WEIGHT (PER CENT.) BY OXIDATION OF PURE AND MIXED OLIVE OIL (*Bishop*).

Number of Hours Exposed.	Olive Oil. Sp. Gr. 0·9155 at 15° C.		
	Pure.	+ 20 °/₀ Arachis Oil.	+ 20 °/₀ Cottonseed Oil.
	Temp. 14°-34·5°.	Temp. 14°-34·5°.	Temp. 14°-34·5°.
24	+0·80	+1·75	+3·25
48	2·40	3·00	4·25
72	3·40	4·00	4·80
144	4·70	4·75	5·60
384	5·30	5·55	6·05
	Temp. 17°-23°.	Temp. 17°-23°.	Temp. 17°-23°.
24	−0·30	−0·30	−0·30
48	−0·20	−0·20	+0·50
72	+0·90	+1·70	2·90
144	2·20	3·10	3·80
264	2·30	3·50	3·90

A summary of Bishop's results is given in the following table:—

TABLE LXXX.

DESCRIPTION OF OIL.	SPECIFIC GRAVITY.	INCREASE OF WEIGHT PER CENT.	MEAN VALUES.
Linseed oil (French), . .	0·9327	17·70–16·40	17·05
„ (La Plata), . .	0·9304	15·45–15·00	15·20
Hempseed oil, . . .	0·9287	14·55–14·30	14·40
Poppyseed oil (French), . .	0·924	14·50–13·90	14·20
Walnut oil, ...	...	13·70	13·70
Cottonseed oil, . . .	0·924	8·60	8·60
„ (chilled), . .	0·923	9·60– 9·30	9·45
Sesamé oil (Senegal), . .	0·9215	8·95– 8·50	8·70
„ (Indian), . .	0·921	7·40	7·40
Arachis oil (African), . .	0·916	6·70	6·70
„ (white), . .	0·916	6·50	6·50
Colza oil (French), . . .	0·9142	6·40 ?	6·40 ?
„ (Indian), . . .	0·9137	5·90–5·80 ?	5·85 ?
Olive oil, ...	0·9155	5·30 ?	5·30 ?

This test deserves further investigation in connection with lubricating oils.

Oxygen Absorption Test.—Dr Angus Smith* in 1870 used the following test in examining some samples of rape oil intended for lubrication. A measured quantity of the oil, from 3–5 c.c., was confined over mercury in a graduated tube filled with oxygen. Absorption took place slowly but steadily during 22 days, when the experiment was stopped and the total volume of gas read off.

	Ratio.
[illegible] oil No. 1 absorbed 3[illegible] c.c.	148
„ „ No. 2 „ 4[illegible] c.c.	187
„ „ No. 3 „ 25·5 c.c.	100

The volumes of oxygen absorbed in the first 48 hours were approximately in the same ratio. Dr Smith considered that the lubricating value of these samples would be in the inverse order of their oxygen absorbing powers.

Fox† has described the following method: About 1 grm. of the oil is sealed up with 0·5 grm. of precipitated lead in a glass tube having a capacity of about 100 c.c. The whole is then heated in an oil-bath for several hours at 105° C., when the amount of oxygen absorbed is estimated by noting the decrease in volume of gas in the tube. The following results were thus obtained :—

Kind of Oil.	c.c. of oxygen absorbed by 1 grm. of oil.
Linseed oil, ...	126 to 191
Cottonseed oil, ...	24·6
Rape oil (brown), ...	20·0
Colza oil, ...	17·6
Olive oil, ...	8·2–8·7

Bach,‡ following Fresenius, has used a similar method, omitting the lead. A known quantity of oil was heated for 10 hours with oxygen in a sealed tube of 100–125 c.c. capacity in an air-bath at 110° C. The point of the tube was then broken under water and the absorbed oxygen calculated from the volume of water drawn in. The results given in Table LXXXI. were thus obtained.

Holde§ describes the following method. From 1–1·5 grm. of freshly ignited pumice stone, in grains about the size of mustard seed, is placed in a glass tube 30–40 cm. long and 20–30 mm. in diameter, sealed at one end, and from 0·3–0·5 grm. of the oil is slowly dropped on to the pumice from a tared beaker; the exact weight added is ascertained by weighing the beaker afterwards. The open end of the tube having been drawn out and allowed to become cold, the air is displaced by oxygen and the tube is quickly sealed with a fine blow-ne. After heating in a water-bath for several hours, the end ube is broken off under water, and the volume of oxygen l is measured. The most suitable temperature and time of

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* Private report. † *Analyst*, viii. (1883), p. 116.

‡ Jour. Soc. Chem. Ind., viii. (1889), p. 990.

§ Die Untersuchung der Schmiermittel, pp. 96 and 100.

TABLE LXXXI.

Kind of Oil.	c.c. of oxygen absorbed by 1 grm. of oil.
l, ...	166
il, ...	144
eed oil, ...	111
il, ...	181
oil, redistilled, so-called cod oil kowitsch),	96·3
l lubricating oil (·865), . . .	4·8
„ (·877), . . .	·7
mineral oil, ...	·74
r and valve oils, ...	·10–·45

depend upon the kind of oil experimented upon. Three ating in a boiling-water bath was used in the experiments, the f which are recorded in the following table :—

TABLE LXXXII.

Description of Oil.	c.c. of oxygen, reduced to 20° C., and 760 mm., absorbed by 1 grm. of oil.	
	Single Values.	Mean Values.
ed oil, ...	68·7	68·7
rape oil, ...	45·5 ; 49·7	47·6
l, ...	33·3 ; 34·0	33·7
of bone oil and refined oil,	32·1 ; 28·1 ; 33·0 ; 28·0	30·3
of bone oil and refined oil,	(29·9); 24·7 ; 22·0 ; 22·2	23·0
il, ...	24·5 ; 23·9 ; 25·3 ; 24·4	24·5
il, ...	18·3 ; 16·6 ; 14·2	16·4

ineral Oils.—Although, as is shewn by Bach's experiments,* ubricating oils are able to absorb small quantities of oxygen ated with it, the amount of oxidation which occurs under conditions is practically nil. The thickening or 'gumming' oils, when it does occur, is due chiefly to the evaporation of volatile hydrocarbons and the concentration of asphaltic,

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o Ostrejko, *Jour. Soc. Chem. Ind.*, xv. (1896), pp. 26, 345, and 645.

TABLE LXXXIII (A).—CHANGES UNDERGONE BY MI

('1 drop' of Oil

No.	Description.	Colour.	Comparative Efflux Velocity at 20° C. (*Engler*). Water=1; Refined Rape oil=12·2.	Specific Gravity at 20° C.	Flashing °C. P=Pe Closed O=Ope
	PALE OILS; TRANSPARENT IN 15 MM. TUBE.				
1	So-called 'paraffin oil,' . .	Colourless	5·9	0·866	158°
2	American 'motor' oil, . . .	Reddish-brown, fluorescent	11·3	..	..
3	Russian heavy machine oil, . .	Reddish-brown	27·6	0·904	185°
4	Heavy machine oil, . . .	Light coloured	66·4 at 15° C.	0·899	205°
5	" . . .	"	33·9	0·903	190°
6	" . . .	"	35·0	0·903	195
7	" . . .	"	42·9	0·905	187
8	Russian heavy machine oil, . .	Reddish-brown	6·2 at 50° C.	0·904	18
	DARK OILS; OPAQUE IN 6 MM. TUBE.				
9	Russian axle oil, . . .	—	45·5	0·906	17
10	Axle oil, ...	—	46·0	0·906	17
11	"	..	37·0	0·907	16
12	"	..	37·6	0·908	17
13	Lubricating oil, ...	..	30·6	0·935	16

ATING OILS WHEN HEATED IN THIN LAYERS (*Holde*).

×10 cm. Glass Plate.)

Condition of Oil Film after heating to							
50° C.				100° C.			
ours.	140 Hours.	190 Hours.	300 Hours.	35 Hours.	70 Hours.	120 Hours.	300 Hours.
com- evap- ; resi- ly.	as before	mere trace of oily residue.	..	all but traces evaporated.	completely evaporated.	..	..
much rated, ptibly ned.	all but traces evaporated; residue oily.	as before	..	greater part evaporated; residue oily.	as before	mere trace of oily residue.	..
anged	unchanged	much evaporated; residue oily.	as before	greater part evaporated; residue oily.	all but trace of oily residue evaporated.	..	..
evap- l,other- un- ed.	greater part evaporated; residue oily.	as before	as before	greater part evaporated; residue oily.	as before	all but oily traces evaporated.	..
anged	much evaporated; residue oily.	as before	the greater part evaporated; residue oily.	..	..	..	..
anged	much evaporated; residue oily.	as before	the greater part evaporated; residue oily.	..	greater part evaporated; residue oily.	..	..
anged	..	partly evaporated; residue oily.	the greater part evaporated; residue oily.	..	..	..	..
wapor- but e oily un- ed.	the greater part evaporated; residue oily.	all but traces evaporated; residue oily.	..	greater part evaporated; residue oily.	all but traces of oily residue evaporated.	..	..
much r.	much thicker	largely evaporated, much thicker.	much evaporated, very thick.	barely fluid, very slightly sticky.	as before	still less fluid	sticky
much med to lightly	much thicker, slightly sticky.	much thicker, slightly sticky.	mostly evaporated; otherwise as before.	..	..	..	..
much med.	as before	as before	much evaporated; oily.	almost dry, oily when warm.	..	..	..
much ned.	much evaporated, considerably thickened.	as before	mostly evaporated; residue oily.	barely fluid to slightly sticky.	as before	as before	very much evaporated, otherwise as before.
much ned.	a little thicker	much evaporated; a little thicker.	much evaporated; thick to sticky.	sticky, barely fluid.	barely fluid, very slightly sticky.	as before	(175 hours), much evaporated, and almost solid even when warm.

resinous, or tarry matters in the residue. Gumming is most marked in the case of the dark residuum-containing oils used for railway and rough work; the refined, pale and charcoal-filtered oils, from which the resinous and asphaltic constituents have been removed, undergo scarcely any change except a thickening due to evaporation when heated.

The results of experiments by Holde,* who has paid considerable attention to this subject, are contained in Tables LXXXIII (A)., LXXXIV (B)., and LXXXV (C)., which shew the behaviour of various mineral lubricating oils when exposed to the air in thin and thick layers at temperatures of 50° and 100° C.

In Table A the behaviour of the pale refined oils is compared with that of the dark 'reduced' oils, and the greater tendency of the latter to thicken and form sticky or 'gummy' residues will be observed.

The results in Table B are intended to shew the behaviour of the very asphaltic Hänigsen petroleum in its crude state and also after the extraction of part of the tarry matter by petroleum spirit and alcohol-ether.

In Table C quantitative results are given, shewing the amount of evaporation resulting from the exposure of mineral oils to 100° C. for several months in thicker layers (0·21–0·24 grm. of oil with a surface of about 75 sq. cm.). The pale, very fluid, and non-resinous 'paraffin oil,' No. 5, from the lowest lubricating oil fractions, gradually evaporated in the course of 15 months, without leaving a trace of resin behind; the more viscous, brownish-yellow 'motor ' oil left a small solid residue, consisting partly of resin originally contained in the oil and partly (as the dark colour of the residue and its insolubility in petroleum spirit proved) of oxidized hydrocarbons formed during the heating. The very viscous oil, No. 7, consisting of a distillate of very high boiling point, evaporated and dried very little; the same oil, partly de-resinified by treatment with alcohol, dried still less. The oils which dried most were the residuum-containing oils, Nos. 1 to 4, of which again those purified with alcohol-ether dried less than the untreated oils. The Russian oil, No. 1, contained, as the viscosity shews, lower boiling hydrocarbons than No. 7, and therefore, although it resinified more quickly than the latter oil, the residue was essentially more fluid. All the resinous residues left by heating mineral oils are incompletely soluble in petroleum ether, even though the original unheated oils (as Nos. 6–8) may have been completely soluble; these residues are, however, easily soluble in benzene.

Holde summarizes the results of his experiments as follows:—When exposed to the air in thin films (1 drop of oil on a 5 × 10 cm. glass plate) the pale and dark-coloured distilled mineral oils do not resinify after several months' exposure, either at the ordinary temperature or when heated to 50° or 100° C. Dark residuum-containing oils by long exposure at ordinary temperatures resinify very little, but at 50°–100° C. a marked thickening, and, with very tarry oils, even complete resinification occurs, whilst the greater proportion of the fluid hydrocarbons evaporate, and the remainder oxidize, adding to the tarry and asphaltic contents of the residue.

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* *Die Untersuchung der Schmiermittel*, pp. 88–99.

In thicker layers (0·20–0·25 grm., exposing a surface area of 75 sq. cm.), the pale-coloured, non-resinous distillates do not resinify even at 100° C., but the dark-coloured distillates, containing 1–3 per cent. of resin, leave partly resinous residues. Dark residuum-containing oils, similarly treated, yield sticky or solid products, even after the first few months, and after 15 months the residues are quite hard and pitchy.

TABLE LXXXIV (B).—BEHAVIOUR OF CRUDE HÄNIGSEN (HANOVERIAN) PETROLEUM HEATED TO 50° C. (*Holde*).

('1 drop' of Oil spread on a 5 × 10 c.m. Glass Plate.)

Previous Treatment.	Consistency at	Number of Hours heated to 50° C.			
		21	42	70	300
None	ordinary temperature	very sticky	sticky, solid	..	..
	40°–50°	oily	very sticky	..	..
Partly freed from asphalt by petroleum spirit ('benzine')	ordinary temperature	very sticky	very sticky	sticky, solid	..
	40°–50°	oily	sticky, scarcely oily	sticky, solid	..
Purified from asphalt by benzine, and from pitch by ether-alcohol	ordinary temperature	moderately sticky	sticky	solid and sticky	solid and sticky
	40°–50°	oily	viscid	viscid	viscid

[illegible]	[illegible]	
[illegible]	176° C. (open)	
[illegible]	0·2100	

[illegible]	Consistence and Appearance.	Total Loss of Weight (grm.).
[illegible]	Solid	0·0444
[illegible]	[illegible]	0·0588
[illegible]	[illegible]	0·0619
[illegible]		[illegible]
[illegible]	[illegible]	[illegible]

LAYERS AT 100° C. (*Holde*).

	5.		6.		7.		8.	
d by :3).	**Russian, colourless, clear, transparent, 'paraffin oil.'**		**American brown-yellow, fluorescent, motor oil.**		**Russian red-brown distillate, made in laboratory.**		**No. 7, deresinified by 70 per cent. alcohol.**	
	5·9		11·6		105·9		..	
	158° C. (*Pensky*)		193° (*Pensky*)		..		..	
	0·2042		0·2430		0·2170		0·2148	
nce nce.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.
l	0·0988	oily, fluid	0·0124	oily	..	oily	..	oily
icky	0·1170	oily	0·0262	..	..	..	..	..
icky	0·1302	..	0·0458	..	0·0024	oily	0·0026	..
icky	0·1522	oily	0·0774	..	0·0109	..	0·0078	..
a lly	0·1622	..	0·0952	..	0·0173	oily	0·0108	..
	0·1727	oily, darkened in colour	0·1114	oily	..	..	..	..
part rest y	0·1846	traces of oily residue	0·1394	greater part waxy, rest greasy	0·0315	viscous oil	0·0204	thick oily, partly solid
and but an 3	0·1876	traces of oily residue	0·1533	solid, brown	0·0330	thick jelly, but part solid	0·0272	viscous, partly solid

7.—SPONTANEOUS COMBUSTION OF OILY MATERIALS.

It is well known that oily rags, oily cotton waste, and similar materials are liable to heat and take fire spontaneously, and that numerous fires have originated in this way; a brief discussion of this subject is therefore of importance to all users of lubricants.

The oxidation of oils is a process in which heat is always evolved, but under ordinary circumstances, the temperature of the oil is not sensibly raised, because the heat, which is evolved slowly, is conducted away as fast as it is liberated. When the rapidity of oxidation is increased by blowing air through a large mass of oil, as in the manufacture of thickened oils, the temperature rises considerably. Conditions most favourable for the generation of heat by oxidation present themselves when a fibrous substance like cotton is saturated with oil and thrown together in a heap, especially in a warm place. Under these conditions the oil, spread out in thin films on the cotton fibres, presents a large surface for oxidation, and the heat being prevented from escaping owing, chiefly, to the absence of convection currents, raises the temperature of the mass and thereby promotes more vigorous oxidation, which leads to a further and more rapid development of heat, until finally the temperature of ignition of the mass may be reached and it bursts into flame.

The subject has been experimentally investigated by Gellatly, Coleman, Young, and many others, by saturating balls of waste fibre with various oils, placing them in a chamber heated to 212° F. or some lower temperature, and noting the time taken by the mass to inflame. The results obtained have shewn that the drying oils, such as linseed, and especially boiled linseed oil, cause ignition most readily, and the non-drying oils least readily, but all drying and semi-drying oils, and even such non-drying oils as olive and lard oil, are capable of causing ignition sooner or later under the conditions named. Mackey has shewn by experiments with olive and cottonseed oils * that free fatty acids are more liable to develop heat and eventually to fire when spread on cotton than the neutral oils themselves,† a fact which he considers of importance in relation to fire risks in woollen mills, as recovered cloth-oils and distilled oleines consist largely of free fatty acids. According to Kissling,‡ the generation of heat is influenced to a considerable extent by the nature of the fibrous material, being most rapid with silk, and less in order with animal wool, cotton wool, jute, and hemp.

In practice, the risk of fire arising from spontaneous ignition of oily material is greater the more readily oxidizable the oil, and therefore, generally, the higher the iodine value of the oil and the greater

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* *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 1164.

† The difference has to do with the chemical action of the fatty acids on the cotton, as it was not observed when an inorganic material like slag wool was substituted for the cotton.

‡ *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 479.

the evolution of heat in Maumené's thermal test. Mineral oils, which are practically incapable of oxidation, do not heat at all, and not only are they, therefore, free from the danger of spontaneous ignition, but, when mixed with fatty oils in sufficient proportion, which varies according to the nature of the fatty oil, they prevent the risk of fire arising from the spontaneous ignition of the mixture. Given a sufficiently high flashing-point, not below 340°–350° F. (171°–177° C.), the more mineral oil there is in a mixed lubricant the safer the oil as regards the liability to cause a fire; nevertheless, the Fire Insurance Companies consider the fire-risk in textile and woollen mills greater the higher the percentage of 'unsaponifiable matter'* in the oil used. This is chiefly owing to the fact that when a fire has once broken out, mineral oils, which, as a rule, flash at a lower temperature than the vegetable oils, are more likely to assist in spreading the fire in proportion to the difference of flashing-point (*Mackey*).

Both in the United States and in this country apparatus has been devised specially for the purpose of determining the relative liability of oils to cause spontaneous combustion.

Allbright and Clark's Apparatus,† generally known as Ordway's, consists of a double chamber, formed by two tubes placed one inside the other. The outer tube is of wrought iron, 6 inches in diameter, and is closed at each end by discs of wood. The inner tube is of sheet iron, 4 inches in diameter, and 6 inches shorter than the outer tube, and is fitted with overlapping metal covers at each end, which support it centrally within the outer tube, leaving an annular air-space of 1 inch between the two tubes and a space of 3 inches at each end. The apparatus, suitably supported, is heated by a Bunsen burner, and three thermometers, which are inserted into the inner tube through the outer, allow the temperature to be read off.

50 grms. of the oil to be tested are distributed as evenly as possible over 50 grms. of cotton waste, which is then carefully pushed into one end of the inner tube, and a second similar ball of un-oiled waste is inserted into the other end. One thermometer is placed with its bulb in the ball of oiled waste, one in the ball of un-oiled waste, and the third midway between the two. The outer tube is then heated so that the thermometer in the un-oiled waste indicates 100°-101° C., not higher, the maintenance of this temperature being controlled by means of the middle thermometer, which should be kept at about 125° C. Spontaneous heating of the oiled waste is indicated by the temperature of the mass rising above that of the un-oiled waste, and the difference of temperature will be greater and the rise more rapid the more dangerous the oil.

Richards states that this apparatus has been of the greatest use in determining the cause of fires and in estimating the relative safety of oils for use in textile mills. Among other results it has been found that the proportions of neatsfoot and best lard oils which can safely be mixed with mineral oil amounts to from 50 to 60 per cent., whilst not more than 25 per cent. of cottonseed oil can be safely added. That is to say, cotton waste oiled with a mixture of 50 per cent. lard oil and 50 per cent. mineral oil would not be liable to ignite spontaneously, but if the lard oil were adulterated with cottonseed oil, ignition might occur. In either case a good deal would depend upon the size of the heap of waste and the temperature of the surrounding air.

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* Mackey, as well as Lewkowitsch, has pointed out the fallacy of assuming the 'unsaponifiable matter' to consist of mineral oil, since in recovered wool grease, for example, it may be composed entirely of cholesterols, and should therefore be examined as described in Chap. VII. p. 219. In distilled wool grease hydrocarbons occur, which, though not 'mineral oil,' are undistinguishable from it, and, as regards fire-risk, may be regarded as identical.

† Richards, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 547.

Mackey's 'Cloth-Oil Tester' (fig. 71)* consists of a cylindrical copper water-bath tinned on the inside, measuring externally 8 inches high × 6 inches in diameter, and internally 7 inches high × 4 inches in diameter, provided with a lid having a short central tube D for a thermometer and two longer tubes A and B for promoting the circulation of air. A cylinder of 24-mesh wire gauze C, 6 inches long × 1½ inches in diameter, contains the oiled wool.

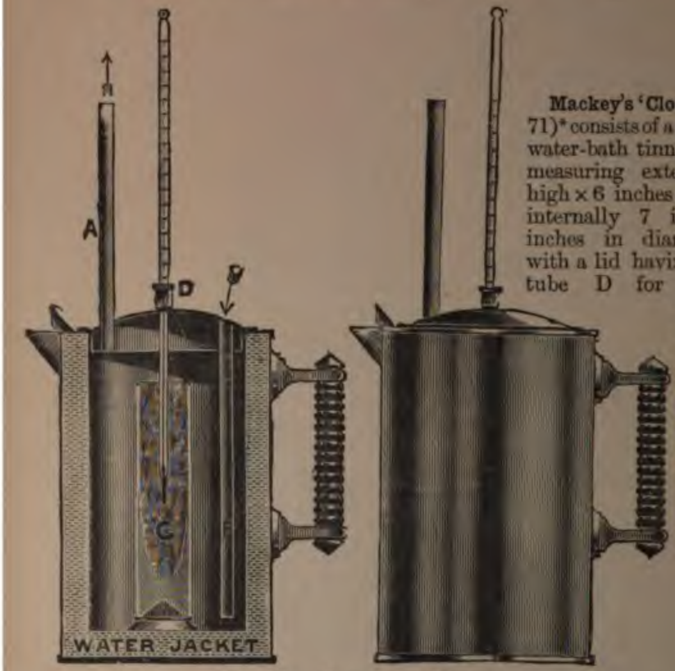

FIG. 71.—CLOTH-OIL TESTER.

14 grms. of the oil to be tested are weighed into a shallow dish containing 7 grms. of pure cotton wool, and after thoroughly incorporating the oil by hand with the well teased wool, which cannot be too carefully done, as the success of the experiment greatly depends upon the even distribution of the oil, the thermometer is held upright in the middle of the gauze cylinder and the oiled wool is carefully and uniformly packed around it. Having raised the water in the outer jacket to active ebullition, the cylinder and thermometer are placed in the inner chamber, the lid is carefully slipped down over the thermometer stem, and the latter is fixed in position by tightening up the screw-clamp D. The position of the thermometer should be such that the red mark on the stem is just visible above D. The water

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* *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 940; and xv. (1896), p. 90.

cket is kept steadily boiling, care being taken that steam is neither own the tube B nor warms the tube A, and the temperature of the ead off at intervals.

ually takes about 1 hour for the oiled wool to reach the ture of the bath (100° C. = 212° F.), and safe oils, like pure l, will not rise much higher; but dangerous oils will con- heat, and very dangerous oils, such as cottonseed, will rise to (392° F.) within one hour and a half. Generally, the tempera- er a certain point is reached commences to rise very rapidly, en this is the case the thermometer must be withdrawn after g say 250° C., otherwise it may be damaged. Mackey states y oil which, when tested in this way, reaches 200° C. in two nay be regarded as too dangerous for use in mills. The worst oil, from a fire insurance point of view, will heat more rapidly is.

one using the apparatus for the first time should experiment re olive and cottonseed oils, comparing his results with those ollowing table by Mackey, until he has found how to prepare k the mixture of wool and oil so as to obtain similar results:—

TABLE LXXXVI.

Oil used.	Temperature in				Maximum.		
	1 hr.	1 hr. 15 m.	1 hr. 30 m.	2 hrs.			
	°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F.	°C = °F.	H.	M.
seed, ...	125 = 257	242 = 468	..	..	242 = 468	1	15
, ...	121 = 250	242 = 468	282 = 540	..	284 = 543	1	35
, ...	128 = 262	212 = 414	225 = 437	..	225 = 437	1	30
, ...	124 = 255	210 = 410	..	..	248 = 478	1	35
, ...	116 = 241	192 = 378	200 = 392	..	200 = 392	1	30
, ...	118 = 244	191 = 376	202 = 396	..	202 = 396	1	30
, ...	117 = 243	190 = 374	194 = 381	..	194 = 381	1	30
, ...	112 = 234	177 = 351	204 = 399	..	211 = 412	1	45
fatty acids, . .	114 = 237	177 = 351	..	..	196 = 385	1	25
, ,, . .	105 = 221	165 = 329	..	..	293 = 559	1	55
, ,, . .	102 = 216	135 = 275	208 = 406	..	226 = 439	1	45
Australian oleine, .	103 = 217	115 = 239	191 = 376	..	230 = 446	1	45
(containing 1 °/o free ty acids),	98 = 208	102 = 216	104 = 219	..	241 = 466	3	25
, ...	98 = 208	101 = 214	102 = 216	..	110 = 230	2	8
leine, . . .	98 = 208	100 = 212	102 = 216	..	172 = 342	3	15
n oleine, . . .	98 = 208	99 = 210	100 = 212	..	173 = 343	3	16
(neutral) . . .	98 = 208	100 = 212	101 = 214	..	235 = 455	5	15
,, . . .	97 = 207	100 = 212	101 = 214	..	228 = 442	4	30
,, . . .	97 = 207	..	101 = 214	..	235 = 455	4	55
, ...	139 = 282	..	..	..	200 = 392	1	4
. . . .	99 = 210	101 = 214	102 = 216	103 = 217	113 = 235	4	30
ure of 50°/o of No. 20 and 50°/o of No. 21	102 = 216	117 = 248	..	..	200 = 392	1	29
ure of 25°/o of No. 20 and 75°/o of No. 21	99 = 210	105 = 221	112 = 234	..	200 = 392	1	52
ure of 10°/o of No. 20 and 90°/o of No. 21	99 = 210	102 = 216	105 = 221	127 = 261	200 = 392	2	9

[illegible]

[illegible]

[illegible] we have made a practice of [illegible] the apparatus [illegible] We have also [illegible] shown in the figure by a [illegible] This prevents the [illegible] bypass an event which otherwise [illegible]

Q.—DETECTION AND ESTIMATION OF ARACHIS OIL IN OLIVE OIL.

Arachis or earthnut oil so nearly resembles olive oil in general characters that the ordinary physical and chemical tests fail to detect its presence. The chief difference lies in the iodine values, which range as under :—

	Lowest.	Highest.
Arachis oil, ...	84·6	105
Olive oil, ...	76·3	88·7 (91·5 ?)

Whilst a high iodine value (say over 85 per cent., which is seldom exceeded by genuine olive oil) might therefore be due to the presence of arachis oil, a normal value is compatible with the presence of this oil in considerable proportion.

Arachis oil, however, contains from 4·3 to 5·4 per cent. of arachidic and lignoceric acids ($C_{20}H_{40}O_2$ and $C_{24}H_{48}O_2$), which, owing to their sparing solubility in cold alcohol, can be isolated without much difficulty. Olive oil contains not more than traces of these acids. Upon this difference in composition, Renard has based the following process for the detection and estimation of arachis oil, which is here described with some modifications in detail introduced by Archbutt.*

10 grms. of the suspected oil are saponified in a basin, as directed in E I. (p. 215), using 8 c.c. of 50 per cent. caustic soda solution and 70 c.c. of alcohol, boiled down gently to about 20 c.c., rinsed with hot water into a separating funnel, decomposed with hydrochloric acid in excess, and shaken with ether to extract the fatty acids. After distilling off the ether in an 8-oz. wide-necked flask, the fatty acids are dried by heating the flask on a steam-bath and sucking out the vapour, and are then dissolved by pouring 50 c.c. of rectified alcohol (sp. gr. 0·834) into the hot flask.

To the solution, which should not be hotter than 110° F., and must not be allowed to cool below 100° F., lest crystals of arachidic and lignoceric acids should separate, 5 c.c. of a 20 per cent. aqueous solution of lead acetate are added, which will precipitate the whole of the arachidic and lignoceric acids as lead soaps, together with some palmitate and oleate of lead.† After cooling to about 60° F. and allowing to stand for about half-an-hour, the alcoholic liquid is decanted through a filter, and the lead soaps are extracted with ether until the washings when shaken in a test-tube with H_2S-water give no colour or only a slight brown ; the soluble lead oleate is thus removed. It is best not to attempt to wash with ether more than once on the filter, but to rinse the soaps back into the flask and digest with ether, then again filter, and again rinse back, using the same filter each time. After doing this about four times, all the lead oleate will have been dissolved out. Washing on the filter takes a much longer time.

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* *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1124.

† This quantity of lead is sufficient for 10 grms. of oil. If more be added, a larger precipitate is produced, containing more lead oleate, which takes more washing out with ether, but no more arachidic and lignoceric acids are obtained ; in fact, if excess of lead be used, as recommended by some chemists, the quantity of these acids recovered is even less, probably owing to the solvent action of the solution of lead oleate in ether on the other lead soaps.

The filter paper containing the lead arachidate, etc., is opened in a large funnel placed in the neck of a separating funnel, and before the soaps have had time to dry they are rinsed into the separator with a jet of ether from a wash-bottle. The soaps which adhere to the paper and flask may be [illegible] and transferred by rinsing with warm dilute hydrochloric acid [illegible] more hydrochloric acid (1·10 sp. gr.) are [illegible] and the mixture is shaken well to decompose the lead soaps, then run off and the ethereal solution of the fatty acids is washed with small quantities of water until the acid is removed. The ether is distilled off in a [illegible] flask, and the residual fatty acids are heated in the water-oven until dry. They are then dissolved by warming with 50 c.c. of 90 per cent. ethyl alcohol [illegible], and the solution is cooled to 15° C., when arachidic acid, if present, will crystallize out, either at once or after standing a short time. The flask should be closed by a cork carrying a thermometer.

According to Tortelli and Ruggeri* a rough estimate of the amount of earthnut oil present may be made at this stage by observing the temperature at which the crystals commence to form. For this purpose the liquid in the flask must be heated until the crystals have re-dissolved, and then allowed to cool slowly.

TABLE LXXXVII.

Temperature at which the crystals commence to form. °C.	Earthnut oil. per cent.
[illegible]	[illegible]
31–33	60
29–31	50
27–28	40
22–24	30
20·5–21·5	20
18–20	10
16–17	5

In order to estimate the proportion of earthnut oil more accurately, the liquid is allowed to stand for 1 hour† with occasional agitation, at 15° C. or 20° C., or at some intermediate temperature which is nearest to that of the laboratory, the crystals are then collected on a small filter placed over a 100 c.c. cylinder, using the filtrate alone to rinse out the flask, and are washed several times with small quantities of 90 per cent. alcohol until the filtrate and washings measure 70–80 c.c., unless the quantity of crystals obtained is very small, in which case less may be used.‡ The filtrate and washings with 90 per cent. alcohol must be measured. The crystals are then washed thoroughly with 70 per cent. alcohol (sp. gr. 0·8898) in which arachidic and lignoceric acids are quite insoluble. These washings are not measured, but the washing is continued until a few c.c. of the filtrate remain clear when diluted with water in a test-tube, shewing that all soluble fatty acids have been washed out. The washed crystals are then dissolved off the filter with boiling ether, distilled down in a tared flask and dried in the water-oven until constant in weight, for which 1 hour or less usually suffices. Finally the melting-point is determined by capillary tube, or preferably by Bensemann's method (p. 195), and the point of incipient fusion should not be lower than 71° C.

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* *Analyst*, xxiii. (1898), p. 273.

† Tortelli and Ruggeri say 3 hours, but Archbutt's experiments shew that 1 hour is enough.

‡ It is a good plan to do this washing with three separate quantities of alcohol, either 10 c.c. or 5 c.c. each according to the size of the precipitate, and, after collecting the washing each time in a small beaker, to pour it back through the filter two or three times, so as to thoroughly saturate it before adding it to the main filtrate. Obviously this must be done at the same constant temperature as that at which the crystallization took place. A paper filter may be used, but a Gooch

Instead of weighing the crystals at this stage, Tortelli and Ruggeri recommend re-dissolving them in 50 c.c. of 90 per cent. alcohol, recrystallizing for 1 hour at the same temperature as before, again filtering and washing, first with 90 per cent. and then with 70 per cent. alcohol, and then weighing. The crystals from pure earthnut oil, when thus purified, melt, by Bensemann's method, at 72·3°–73·3° C.* This recrystallization is not, however, necessary, unless the melting-point of the first crop is too low or the quantity of crystals large.

As the arachis acids are slightly soluble in the 90 per cent. alcohol used for recrystallization and washing, a correction must be made, which varies according to the weight of mixed acids obtained (*Tortelli* and *Ruggeri*). This correction is given by the following table:—

TABLE LXXXVIII.

Weight of Mixed Acids obtained. *Grm.*	Correction (grm.) to be added per 100 c.c. of 90 per cent. alcohol used, at		
	15° C.	17·5° C.	20° C.
0·9 and upwards.	0·071	0·081	0·091
0·8	0·070	0·080	0·091
0·7	0·069	0·079	0·090
0·6	0·067	0·077	0·088
0·5	0·064	0·074	0·085
0·4	0·061	0·070	0·080
0·3	0·055	0·064	0·074
0·2	0·048	0·056	0·064
0·1 and less.	0·033	0·039	0·046

The percentage of arachis acids thus isolated from pure earthnut oil by Renard, De Negri and Fabris, Tortelli and Ruggeri, and Archbutt, has varied from 4·28 to 5·40 per cent.; averaging about 4·8 per cent. Therefore, the weight of arachis acids obtained, multiplied by 21, is approximately equal to the weight of arachis oil in the quantity of oil taken for experiment.

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filter used with moderate suction is better, because the crystals can be more completely separated from the mother liquor.

* Tortelli and Ruggeri found the melting-point of the recrystallized acids, determined by capillary tube, between 74° and 75·5° C.

The following results show the degree of accuracy attainable by this method. [illegible] grms. of oil were taken for the analysis in each case, and the arachis acids were not recrystallized.

TABLE [illegible]

Composition of the mixture per cent.		Volume of 90% alcohol. Temperature. Solubility coefficient.	Mixed arachis acids.					Arachis oil found per cent.
[illegible]	[illegible]		Dissolved in the alcohol.	Weighed.	Total.	Per cent.	Melting-point in capillary tube °C.	
	100.	[illegible] c.c. 17 [illegible] ·063	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	100
50	50	73 c.c. [illegible] C. ·033	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	102
[illegible]	20	73 c.c. 15° C. ·033	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	102

The correctness of the method has also been proved by Renard, by De Negri and Fabris, and by Tortelli and Ruggeri. The latter chemists, working on 20 grms. of oil and recrystallizing the arachis acids, obtained the following results:—

Arachis oil taken, per cent. . .	60	50	40	30	20	10	5
Arachis oil found, per cent. . .	60	50	40	31	22	11	6·7

Reimer and Will found in rape oil an acid of high melting-point, sparingly soluble in alcohol, which they believed to be behenic acid, $C_{22}H_{44}O_2$. Ponzio subsequently identified this acid as arachidic; but judging by the solubility in alcohol and the melting-point, it is probably a mixture of arachidic and lignoceric acids. Archbutt has isolated these acids from 33 out of 51 samples of commercial rape oil and has proved that the quantity present may amount to as much as 1·43 per cent. He has also found the same acid in mustard oil.* It appears from these results that the fact of finding arachis acids in olive oil is not conclusive proof of the presence of earthnut oil, unless rape and mustard oils are proved to be absent by other tests, of which the saponification value is the most important. Unless the saponification value of a sample of olive oil is below 19·0, neither rape nor mustard oils are likely to be present.

R.—COLOUR REACTIONS.

Most of the colour reactions which formed such a prominent feature of the older works treating of oil analysis have been shewn to be caused not by characteristic constituents of the oils themselves but by impurities which are more or less perfectly removed in the processes of refining; and many of these reactions, based upon tests made with a limited number of specimens of oil, have been found by more extended experience to be valueless. Although the quantitative methods developed during recent years have made us much less dependent than formerly upon colour tests, the means of identifying oils in mixtures are still imperfect, and such colour reactions as are undoubtedly produced by natural constituents of particular oils, of which there are a few, are valuable.

I. Reactions of Cottonseed Oil.

(*a*) **The Nitric Acid Test.**—This test is given in the form recommended by Lewkowitsch.† Oils containing cottonseed oil, when shaken, cold, with an equal volume of nitric acid of sp. gr. 1·375, develop on standing for a short time a characteristic coffee-brown coloration, the intensity of which is in proportion to the amount of cottonseed oil present. Stronger acid gives less definite results.

In applying this test to a sample of oil, the colour obtained should be compared with that given under the same conditions by a pure sample of the same kind of oil. The test is most useful in the case of olive oil which, when pure, is scarcely changed in colour by the nitric acid. In consequence of an observation by Holde that refined rape oil when shaken with nitric acid of 1·41 sp. gr. also gives a brown colour, Lewkowitsch mixed a large number of samples of olive oil with varying proportions of cottonseed oil on the one hand and rape oil on the other and shook them with nitric acid of 1·375 sp. gr. After standing for 24 hours, the two sets shewed striking differences of colour; those containing cottonseed oil were of a pale brown colour, whilst those mixed with rape oil became more yellowish. Archbutt has been unable to confirm this observation. In a similar series of tests he found, with one sample of rape oil, that although no brown colour was developed within 40 minutes whilst the mixtures, containing 5 per cent. and upwards of cottonseed oil, all gave a distinct brown colour in the same time, on longer standing the mixtures containing rape oil also become brown in colour, and before the end of 24 hours could not be distinguished in shade from those containing cottonseed oil. Another sample of refined (Stettin) rape oil, undoubtedly genuine, when mixed in the proportion of 20 per cent. with the same sample of olive oil as was used in the above tests, gave a brown colour in 40 minutes which could not be distinguished from the colour given by 20 per cent. of cottonseed oil. A more extended experience has confirmed the fact that many genuine rape oils give a brown colour when shaken with nitric acid of 1·375 sp. gr.

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* *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1009.

† *Analysis of Oils, etc.*, p. 381.

Some genuine lards have been found to give a brown colour with nitric acid; but this should not mislead an experienced analyst, as the presence of cottonseed oil ought not to be certified unless it is confirmed by quantitative tests, such as the iodine value of the sample. The reaction with nitric acid has this advantage over the following, silver nitrate, test, that the brown colour is obtained with cottonseed oil which has been heated to 240° C., as well as with oil which has not been heated. Lewkowitsch states, however, that some American cottonseed oils which he has met with gave such a faint coloration with nitric acid that 10 per cent. could not be detected in olive oil by this test; but such oils are rare.

It may be noted that blown oils, both rape and cotton, even if present to the extent of only 10 per cent., give a very intense red-brown colour when shaken with nitric acid.

(*b*) **The Silver Nitrate Test.**—This test, originated by Becchi, depends upon the presence in cottonseed oil of a substance which reduces silver nitrate. If the oil be saponified and the fatty acids isolated, they give the same reaction. In Becchi's test, the oil is heated with a complex reagent containing an alcoholic solution of silver nitrate, ether, nitric acid, amyl alcohol, and rape oil; but it is preferable to employ for the test a solution of the fatty acids in pure alcohol, as proposed by Milliau, omitting the amyl alcohol and rape oil. The following method of procedure is recommended:—

Approximately 5 grms. of the oil are saponified as directed in E I. (p. 215). The alcoholic soap solution, concentrated to about 10 or 15 c.c., is diluted with hot water, rinsed into a separating funnel, decomposed with excess of dilute sulphuric acid, and shaken with about 70 c.c. of ether to dissolve the fatty acids. After drawing off the aqueous liquid, the ethereal solution is washed 4 or 5 times with small quantities of cold water and poured into a flask. The ether is then distilled off, and the flask containing the fatty acids is heated on a steam-bath for a few minutes to evaporate the remaining traces of ether and water.

The fatty acids thus obtained are immediately dissolved by pouring 20 c.c. of absolute alcohol into the flask, and the solution is poured into a dry test-tube measuring 8 inches × 1 inch. The contents of the test-tube are raised to boiling by cautiously heating over a small Bunsen flame, and then, whilst holding the test-tube over a white tile, 2 c.c. of a 30 per cent. aqueous solution of silver nitrate are added from a pipette. In the presence of 5 per cent. of cottonseed oil, a characteristic brown turbidity is produced almost immediately. The reaction is more rapid and intense the greater the proportion of cottonseed oil present. If there be no immediate reduction, the solution is kept under observation for a minute or two at boiling-point, by moving the tube to and fro from the tile to the flame, and if only 2 per cent. of cottonseed oil be present a distinct reaction, though more slowly developed, will be obtained.

This reaction has been examined by a large number of chemists and found to be quite characteristic of cottonseed oil. Archbutt has applied the test to a large number of olive oils and tallows without ever observing the slightest reduction of the silver by samples known to be genuine, or which were proved to be so by quantitative tests. Some genuine rape oils appear to reduce the silver very slightly, but the reaction takes place slowly, and the colour produced is blackish, whilst with cottonseed oil it is brown. Possibly in these cases the precipitate is sulphide of silver, due to sulphur in the rape oil. In testing fats which have been exposed to the air, or have become rancid, it must be remembered that aldehydic bodies formed by oxidation may reduce the silver solution. Thus Bevan* found that lard which had been exposed to the air for some days gave Becchi's reaction, whilst some of the same lard taken from the interior of the mass had no reducing property. Hehner† states that genuine butter made from the milk of cows fed largely on cottonseed cake frequently gives the reaction of cottonseed oil.‡

Since it is not known whether all samples of cottonseed oil reduce silver nitrate to the same extent, it is not safe to draw quantitative conclusions from this test; but an estimate of the proportion of cottonseed oil based upon the result of the colour test generally agrees fairly well with that calculated from the quantitative results.

Allen, Wiley, Rowland Williams, Stock and others have obtained good results by the Milliau Test. Lewkowitsch has found the results to be erratic, and prefers Becchi's original method. This different experience may be due to the fact that the fatty acids if kept heated even to 100° C., and especially if washed with boiling water, gradually lose their reducing property.

Thus the fatty acids obtained from a mixture of rape oil with 5 per cent. of cottonseed oil, which reduced silver nitrate immediately when first tested, completely lost the property by heating in the water-oven for 1 hour. 50 grms. of pure cottonseed oil were saponified and the fatty acids were obtained. After transferring 5 c.c. to a test-tube, the remainder of the acids were placed in the water-oven in a wide beaker, and at intervals of 1 hour 5 c.c. were taken out and transferred to tubes. The different quantities were then tested together and the amount of reduction compared. The fatty acids which had not been heated reduced the silver very strongly, the remaining quantities had a reducing power which diminished progressively according to the length of time they had been heated, and after heating for 9 hours it was estimated that about 95 per cent. of the reducing action had been lost.

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* *Analyst*, xix. (1894), p. 88.

† *Ibid.*, p. 89.

‡ Confirmed later by experiments made on behalf of the Board of Agriculture. See *Analyst*, xxiii. (1898), p. 255.

A more rapid loss of the reducing property occurred when the fatty acids were repeatedly boiled with water. Thus, some fatty acids from pure cottonseed oil which reduced silver very strongly were boiled with water for 1 hour in a basin; the reducing property, though still strongly marked, had decidedly diminished. The same fatty acids were then boiled four times successively, for only one or two minutes each time, with fresh quantities of water, when they were found to have lost from 85 to 90 per cent. of their original reducing power.

From these results it is evident that if the fatty acids for the Milliau test are prepared in the ordinary way, viz., by acidifying the hot soap solution in a basin, heating until the fatty acids are clear, washing with hot water and drying in the water-oven, erratic results may be expected. But by separating the fatty acids with ether in the manner described on p. 278, and by avoiding more than 10–15 minutes' heating to expel the ether, the results are perfectly reliable.

Cottonseed oil which has been heated to 240° C. no longer responds to either Becchi's or Milliau's tests.

(*c*) **Halphen's Reaction.***—Oils containing cottonseed oil, if heated with carbon disulphide, free sulphur, and amyl alcohol, develop a characteristic rose-red coloration, the depth of which is in proportion to the amount of cottonseed oil present. The relative proportions of oil and reagents, and the method of heating, may be varied without interfering with the test, as is evident from the different directions given by different analysts. The following method will be found quite satisfactory:—

3 c.c. of the oil, 1 c.c. of a 2 per cent. solution of sulphur in carbon disulphide, and 1 c.c. of amyl alcohol are mixed in a small test-tube, which is then heated in a bath of boiling water. With as little as 5 per cent. of cottonseed oil present, a distinct rose-red coloration is developed in from 15 to 30 minutes; the colour is more intense and more rapidly produced the larger the proportion of cottonseed oil. Less than 5 per cent. can be detected if the heating be continued for 1 hour, and if the colour be then compared with that of a pure sample of oil tested at the same time. Archbutt has found this test to be quite trustworthy and very delicate.†

II. Reaction of Sesamé Oil.

Badouin's Reaction.—Sesamé oil contains a substance which produces a rose-red coloration when the oil, either pure or in admixture with other oils, is shaken with a solution of cane sugar in hydrochloric acid.

In making the test, 0·1 grm. of pure cane sugar is first dissolved in 5 c.c. of cold, strong hydrochloric acid (1·16 sp. gr.), 10 c.c. of the oil are then added, the tube is corked, shaken for 10 minutes, and allowed to stand. If only 2 per cent. of sesamé oil is present, the acid which separates will be pink in colour. If 5 per cent. and upwards be present there will be no need to shake for 10 minutes, as the emulsion will be observed to become pink while it is being shaken.

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* *Analyst*, xxiii. (1898), p. 131.

† See also *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1075.

Several foreign observers have found that in the case of certain olive oils of undoubted purity the acid liquid assumes 'after a short time' a violet coloration.* Villavecchia and Fabris † further state that some genuine Italian olive oils give a red colour similar to that produced by sesamé oil. We have confirmed this latter observation in testing a few genuine olive oils, but the pink colour observed by us has always been very faint. If, after 10 minutes' shaking, the acid which separates is not distinctly pink or red in colour, sesamé oil should be assumed to be absent, and no notice should be taken of any colour which develops on standing. In any case, error is not likely to occur so long as the results of this test are supported by the results of the quantitative reactions. Milliau has found that if the test be applied to the fatty acids instead of to the oil, any possible error is obviated, and this has been confirmed by other chemists.‡ Therefore, Milliau's method should be adopted in any case where doubt exists as to the cause of the coloration. Villavecchia and Fabris § find this colour reaction to be due to *furfurol*, produced by the action of hydrochloric acid on sugar, and they have accordingly proposed to employ a solution of furfurol instead of cane sugar. As furfurol itself gives a violet coloration with hydrochloric acid, a very minute quantity must be used.

For the test, a 2 per cent. solution of furfurol in alcohol is prepared. 0·1 c.c. of this solution is placed in a tube, 10 c.c. of hydrochloric (1·16) and 10 c.c. of the oil are added; the tube is then corked, shaken for half a minute, and allowed to stand. If even 1 per cent. of sesamé oil be present, the acid which separates has a pink coloration, with 5 per cent. a strong rose-red colour is obtained. This test is recommended, as it is simpler than the test with sugar, and half a minute's shaking is quite sufficient.

III. Reactions of Cholesterol and Phytosterol.

(*a*) **With Chloroform and Sulphuric Acid** (*Hesse, Salkowski*).—If a few centigrammes of cholesterol be dissolved in 2 c.c. of chloroform and the solution be shaken with an equal volume of sulphuric acid of 1·76 sp. gr., the chloroformic layer at first becomes pink, deepening more or less rapidly (according to the quantity of cholesterol present) to blood-red, then cherry-red or purple, the latter colour persisting for some time and changing to a mahogany tint on prolonged standing. If some of the purple solution be poured into a porcelain basin, the colour soon fades to a dirty green and ultimately yellow, but the

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* Lewkowitsch, *Analysis of Oils, etc.*, p. 390.

† *Jour. Soc. Chem. Ind.*, xii. (1893), p. 67.

‡ *Ibid.*, xvii. (1898), p. 275.

§ *Ibid.*, xiv. (1894), p. 69.

[illegible]

[illegible]

(a) The [illegible] Reaction.*—[illegible] This reaction is [illegible] even by [illegible]

To detect rosin oil in mineral oil, 2 c.c. of the sample are shaken [illegible] in a dry test-tube with about 3 c.c. of acetic anhydride [illegible] and allowed to separate. After cooling, the acetic anhydride [illegible] drawn off with a fine pipette and transferred to another tube, or, preferably, the liquid is poured on to a small filter previously moistened with acetic anhydride, when the oil will remain on the filter and a bright filtrate will be obtained. To this filtrate one drop of sulphuric acid of sp. gr. 1·53 is added, and in the presence of rosin oil an immediate, very fugitive coloration, varying from violet-red to cherry-red, is obtained. Pure mineral oil gives a yellow or brown colour, which is sometimes so dark as to obscure the rosin oil reaction. In such cases, the test may be made more delicate by pouring one drop of the acetic anhydride filtrate into another tube before adding sulphuric acid; on diluting this with 1 or 2 c.c. of acetic anhydride and adding one drop of sulphuric acid to the diluted liquid, the violet coloration is more plainly seen. 5 per cent. of rosin oil may be thus detected. Morawski points out that the dark coloration of mineral oil with sulphuric acid is intensified by the application of too much heat in shaking the oil with acetic anhydride, and that if the extraction be done cold a paler colour will be obtained and the rosin oil reaction will be less obscured.

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* *Jour. Soc. Chem. Ind.*, vii. (1888), pp. 135, 136.

Owing to the fact that cholesterol and phytosterol also give a violet coloration with sulphuric acid in acetic anhydride solution, Storch has stated that this test cannot be relied upon for the detection of rosin oil in the presence of fatty oils; but Morawski has found that the test is applicable to most vegetable oils, which, when pure, give only green, yellowish, or yellowish-brown colorations. If, therefore, the presence of rosin oil in a fixed oil be suspected, the coloration obtained should be compared with that yielded under similar conditions by a pure sample of the same fixed oil. In the case of oils such as shark-liver and others which, owing to the presence of cholesterol, do interfere with the test, Lewkowitsch suggests that the oil should be saponified, and after extraction of the unsaponifiable matter (including cholesterol) with ether, the fatty acids liberated from the soap solution should then be tested for resin acids, which always accompany rosin oil. If the sample under test contains added rosin or rosin soap, this device of course fails; rosin oil must then be searched for in the unsaponifiable matter by other tests.

(*b*) **Holde's Test.**—According to Holde,* if 5 c.c. of oil be vigorously shaken in the cold with 5 c.c. of sulphuric acid (1·60 sp. gr.) the acid layer which separates assumes a distinct red colour in the presence of rosin oil. The vegetable and animal oils and most mineral lubricating oils impart only a faintly yellow to yellowish-brown or grass-green colour to the acid. Various kinds of fish oil, imperfectly refined mineral oils, also tar oil, cause a dirty brown-red coloration of the acid; and, in such cases, the detection of rosin oil by means of this reaction is only made possible by extracting it with 90 per cent. alcohol and mixing the alcoholic extract in a test-tube with a small quantity of sulphuric acid of 1·53 sp. gr., which is allowed to flow down the side of the tube.

Holde states that 1 per cent. of rosin oil can be detected by this reaction, but our experience is that the test is decidedly less delicate than the Liebermann-Storch reaction. Pure rosin oil certainly gives a very characteristic bright red colour, which distinguishes it at once from pure mineral oil, but comparative experiments with pure mineral oil and mixtures of the same with rosin oil in different proportions shewed that the mixture containing 5 per cent. of rosin oil gave only a very slightly redder colour than the mineral oil alone. The difference was distinct with 15 per cent., and still more so with 20 per cent. of rosin oil, but the reaction could not be depended upon for the detection of 10 per cent. except by making a blank experiment simultaneously with the pure mineral oil. Shark liver oil and seal oil gave a red-brown colour, as [illegible] [illegible]. Refined rape oil scarcely coloured the acid, but with blown rape the whole mixture became nearly black in colour and the red could not be distinguished from the oil.*

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* *Die Untersuchung der Schmiermittel*, p. 115.

7. Detection of Resin Acids (Rosin).

The Liebermann-Morawski Reaction.—If a few milligrams of colophony be dissolved by warming in 2–3 c.c. of acetic anhydride and the solution be made quite cold, on adding *one drop* of sulphuric acid of 1·53 sp. gr. and shaking, a pure violet colour is produced, slowly fading to a neutral tint. With concentrated acid the colour is redder, and if the liquid be heated (*e.g.*, by adding several drops of acid as in testing for cholesterol) the colour changes to brown or yellow.

To detect rosin in an oil, fat, or grease by means of this reaction, the substance should first be saponified and the soap solution shaken with ether to remove unsaponifiable matters, especially rosin oil and cholesterol. The fatty acids are then obtained from the soap solution and a small portion is dissolved in acetic anhydride in the cold, or at a very gentle heat. The solution, having been made quite cold, sulphuric acid of sp. gr. 1·53 is allowed to flow down the side of the tube, and in the presence of resin acids a coloration ranging from violet to violet-red is produced where the liquids mix. Lewkowitsch recommends this test as thoroughly trustworthy in all cases.

8.—DETECTION AND ESTIMATION OF ROSIN OIL IN MINERAL OIL.

(a) **The Liebermann-Storch Colour Test.** (See p. 282.)

(b) **The Acetone Test.**—According to Demski and Morawski,† rosin oils mix with acetone in nearly all proportions, whilst mineral oils require several times their volume of acetone to effect complete solution. If, therefore, an unsaponifiable oil gives a clear solution with an equal volume of acetone, it is either a pure rosin oil or a rosin oil with very little mineral oil; if an insoluble residue remains it consists of mineral oil. Wiederhold,‡ who has proposed the same test, states that the acetone must be dry and free from alcohol, but that the presence of aldehyde is of no importance. The difference between the solubility of rosin oil in moist and in dry acetone is very considerable. Rosin oil will dissolve in half its volume of *dry* acetone at 15° C.

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* [illegible] Jour. Soc. Chem. Ind., ix. (1890), p. 419, and [illegible]

† [illegible]

‡ [illegible] Chem. Ind., xii. (1893), p. [illegible]

(*c*) **Finkener's Test.**—Finkener * has proposed the use of a solvent prepared by mixing, at 15·5° C., 10 volumes of alcohol of sp. gr. 0·8182 with 1 volume of chloroform. Rosin oil dissolves in from 10 to 12 volumes of this mixture at 23° C., whilst mineral oils are not completely soluble even in 100 volumes. Occasionally rosin oil is met with which, when dissolved in 10 volumes of the mixture and allowed to stand for several hours at 23° C., deposits an oily sediment amounting to from 3 to 7 per cent. of the rosin oil taken, but if 12½ volumes of the mixture be used instead of 10 volumes, any insoluble residue then obtained may be assumed to be mineral oil. Wiederhold † considers that the necessity of working at 23° C. renders the above test impracticable, and he states that if 16 volumes of the chloroformic alcohol be used the test may be made at a temperature of 15° C.

(*d*) **Polarimetric Test.** — According to Valenta, most rosin oils are strongly dextrorotatory, the rotation varying from 30° to 40° in a 100 mm. tube. Demski and Morawski observed a rotation of about 50°. The rotation of seven samples examined by Pelgry at the Charlottenburg Versuchsanstalt varied from 32° to 42°.‡ On the other hand, pure mineral oils are, as a rule, optically inactive, one sample only having been found to give a rotation of + 1·2°. Dark coloured oils must be decolorized by filtration through animal charcoal.

(*e*) **Estimation of Rosin Oil by Storch's Method.**§—According to Storch, rosin oil mixes with absolute alcohol in all proportions, but the presence of a comparatively small proportion of water greatly reduces the solubility. Thus, 96 per cent. alcohol dissolves from 11·3 to 16·2 per cent. of rosin oil, whilst 90 per cent. alcohol dissolves only from 2·6 to 4·0 per cent. Mineral oil, on the other hand, is much less soluble than rosin oil. Upon this difference of solubility, Storch has based the following method for the estimation of rosin oil when mixed with mineral oil:—

10 grms. of the mineral oil, which has been proved by the foregoing tests to contain rosin oil, and which must be quite free from fatty oils, are gently warmed with 50 grms. of 96 per cent. alcohol (sp. gr. 0·8123), then well shaken and allowed to cool. All the rosin oil, even if 50 per cent. be present, will now be dissolved in the alcohol, together with some of the mineral oil. The alcoholic solution having been carefully drawn off with a fine pipette and transferred to a small Erlenmeyer flask about seven cm. high, the surface (only) of the undissolved mineral oil is rinsed with a few c.c. of 90 per cent. alcohol, which is also transferred to the flask. The latter is then placed on a water-bath, surrounded by a bottomless beaker, and the alcohol is gently boiled off.

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* Holde, *Die Untersuchung der Schmiermittel*, p. 116.

† *Analyst*, xviii. (1892), p. 207.

‡ Holde, *Die Untersuchung der Schmiermittel*, p. 118.

§ *Jour. Soc. Chem. Ind.*, vii. (1888), p. 136 ; *Analyst*, xiii. (1888), p. 71.

[illegible] dried and weighed. [illegible] of the spirit in this way the [illegible] is greater [illegible] Residue *A* is next warmed and [illegible] weight [illegible] per cent. [illegible] and the solution is again [illegible] contained the [illegible] The weight [illegible] difference is the weight of [illegible] that this [illegible] result is more nearly [illegible] weight of residue *B*.

EXAMPLE.

[illegible] per cent. of rosin oil were taken.

		Grms.		Grms.
[illegible]	[illegible]	[illegible]	Residue *A*.	1·5136
[illegible]	[illegible]	[illegible]	„ *B*.	1·1584
[illegible]	[illegible]	[illegible]	Mineral oil.	·3552

[illegible] grms. mineral oil and [illegible] ·3580 grms. of [illegible] which is not far from the

Estimation by McIlhiney's Method.*—This method depends [illegible] heated with rosin oil, converts it [illegible] mineral oil is not much affected. The [illegible] petroleum ether, in which the mineral oil [illegible]

[illegible] heated to boiling in a flask of 750 c.c. [illegible] grms. of the oil are dropped in. The [illegible] frequent shaking, for 15 to 20 [illegible] then cooled, and the liquid is made [illegible] is then dissolved by shaking with [illegible] distilled off in the usual manner, [illegible] As mineral oils lose about 10 per cent. [illegible] divided by 0·9, gives the amount of [illegible] taken. A mixture consisting of 76 per [illegible] per cent. rosin oil gave, by this method, 76·8 per [illegible]

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* Journ. Soc. Chem. Ind., xiv. (1895), p. 198.

T.—ESTIMATION OF PARAFFIN IN MINERAL OILS.

The following method * is due to Holde (after *Engler* and *Böhm*). It will seldom be required, but may occasionally be found useful.

10 to 20 c.c. of oils poor in paraffin (Russian distillates, etc., setting below – 5° C.), or 5 grms. of such as are rich in that constituent (American, Scotch, or Galician oils setting at or above 0° C.), are treated, at the ordinary temperature, with a mixture of 98·5 per cent. alcohol and anhydrous ether (1 : 1) until a clear solution is obtained. The liquid is cooled in a freezing mixture of ice and salt to about – 20° to – 21° C., when more alcohol-ether is gradually added, with thorough agitation, until no oil drops, but only solid paraffin flakes or crystals, remain in suspension, and then, while still cooled to at least – 19° to – 21° C., the liquid is poured on to a chilled 9 cm. filter paper, previously moistened with the alcohol-ether mixture, which is contained in the apparatus shewn in fig. 72. The precipitate is washed with cold (– 19° to – 21° C.) alcohol-ether (1 : 1; or for soft paraffin 2 : 1) at a temperature as much below – 15° C. as possible. In the case of soft paraffin, the temperature should average – 18° to – 19° at the highest. In washing the precipitate it is repeatedly stirred up, and as soon as 5–10 c.c. of the filtrate leaves on evaporation only a trace of fatty or paraffin-like residue, solid and not oily at the ordinary temperature, the washing is discontinued. If any doubt exists as to the paraffin being thoroughly freed from oil, or if the washing takes too long, the filter should be removed to another funnel, and the contents dissolved into a small flask with the least possible quantity of benzine. After evaporation of the benzine, the paraffin is redissolved in 4 to 5 c.c. of warm ether, which is then mixed with twice its volume of absolute alcohol, vigorously stirred, and cooled to – 18° to – 20° to reprecipitate the paraffin, which is again filtered and washed, as already described, until free from oil. This reprecipitation is necessary for oils containing much soft paraffin, otherwise so much liquid is used in washing the precipitate that an appreciable quantity of paraffin is dissolved. The purified paraffin is finally dissolved into a tared flask with hot benzine or ether, which is distilled off, and the residue is heated on the steam-bath until the smell of benzine or ether has disappeared. The flask is then heated inside the water-oven for ¼ hour and weighed when cold. Prolonged heating causes loss of paraffin. The whole operation occupies from 1 to 2 hours. Duplicate results with the

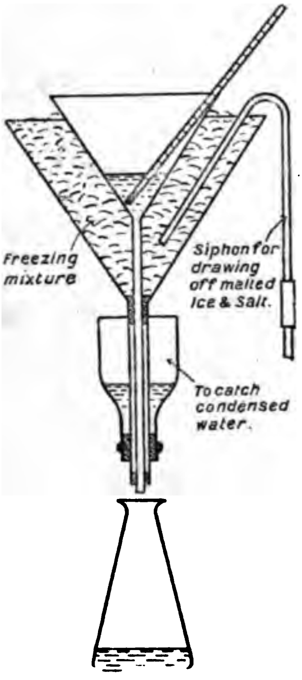
Freezing mixture
Siphon for drawing off melted Ice & Salt.
To catch condensed water.

FIG. 72.—ESTIMATION OF PARAFFIN.

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* *Jour. Soc. Chem. Ind.*, xvi. (1897), p. 362.

same sample agree within 0·23 per cent. for hard paraffin and 0·33 per cent. for soft paraffin. Two samples of Russian machine oil yielded 0·34 per cent. and 0·36 per cent. of paraffin respectively. An American spindle oil, fluid but thick at −2° C., and which set at 0° C., was found to contain 4·11 per cent. of paraffin.

U.—ASPHALT AND RESIN IN MINERAL OILS.

Such slight tendency to 'gum' and form sticky or resinous deposits as is possessed by pure mineral lubricating oils is attributed by Holde* to the presence of dissolved substances of a resinous, asphaltic, or pitchy nature, which gradually accumulate in and thicken the oil film whenever the conditions of working are such that evaporation of the fluid constituents of the oil can take place. These substances are composed chiefly of carbon and hydrogen, with small quantities of oxygen and sulphur, and are regarded by Engler as oxidation products. They occur chiefly in the dark-coloured 'reduced' oils; in the processes of distillation and refining to which the pale oils are subjected they are for the most part eliminated. Holde divides them into three classes:—

1. **Resins, soluble in 70 per cent. Alcohol.**—These substances, which are obtained by shaking the oil with 70 per cent. alcohol and evaporating the solution, resemble colophony in appearance; but instead of giving a violet colour in Morawski's test with acetic anhydride and sulphuric acid (p. 284), a yellowish-brown or dirty-brown colour is produced. Some have acid characters and soap-forming properties; others are neutral. According to Holde, badly refined mineral oils may contain as much as 3·5 per cent. of these resins; but, as a rule, the proportion does not exceed 0·6 per cent. in pale oils and 1 per cent. in dark oils. Some of these resins are soluble in petroleum spirit, others are insoluble, but they all dissolve completely in alcohol-ether (4 : 3 and also 3 : 4).

2. **Asphalt, insoluble in Petroleum Spirit.**—Bender † found that dark-coloured mineral oils, when dissolved in petroleum spirit and allowed to stand, deposit a substance which, when collected, washed, and dried, is a fine powder resembling dark brown coal in appearance, having a slightly bituminous smell and burning with a smoky flame. This substance dissolves easily in benzine, and is of the nature of [illegible] [illegible] is that the amount of asphalt thus obtained from [illegible] [illegible] the sp. gr. and boiling point of the [illegible] being largest with spirit of low boiling point; [illegible] of spirit used, which should be large; and [illegible] should be at least 24 hours. The [illegible] dissolved and not suspended in the [illegible] [illegible] dark oils are mainly paraffin [illegible]

[illegible] 1896, p. [illegible]

with asphalt), at first dissolves along with the oil in the petroleum spirit; only on standing does it separate out, and the less there is in the oil the longer it takes to precipitate. Holde states that, except as a colouring agent, the influence of this asphalt at ordinary temperatures is small; but when the oil is used at temperatures and under conditions in which the fluid hydrocarbons can evaporate, the asphalt and resins accumulating in the film cause it to become thick and sticky, and ultimately dry and resinous. The largest amount of asphalt, amounting to 5 or 6 per cent., is found in German (Alsatian and Hanoverian) oils; the smallest quantity is met with in American and Russian oils.

3. **Asphalt-Pitch insoluble in Alcohol-Ether** (4 : 3).—By dissolving dark mineral oils in a mixture of alcohol and ether, Holde has obtained as an insoluble residue this substance, which includes the asphalt precipitated by petroleum spirit, but is much more fusible, resembling soft pitch. The amount obtained from a given oil increases with the proportion of alcohol in the solvent. With the 4 : 3 mixture, the amount of asphalt-pitch obtained from Russian oil ranged from 0·16 per cent. in a distilled machinery oil to 5·7 per cent. in a railway oil; a thick lubricating oil from Oelheim gave 11·1 per cent., and a very thick crude petroleum from Wietze gave 15·4 per cent.

For the detection and estimation of these substances, Holde proceeds as follows:—

(*a*) *Estimation of Resin soluble in 70 per cent. Alcohol.*—8–10 c.c. of the oil are well shaken in a test-tube with an equal volume of 70 per cent. alcohol (sp. gr. 0·8898), the mixture being heated. It is then made quite cold. After complete separation has taken place the alcoholic liquid is drawn off, without loss, and evaporated to dryness in a tared beaker containing a glass rod. When perfectly dry and cold the consistency of the residue is ascertained by feeling it with the glass rod, and if sufficient in amount to be worth weighing, it is weighed. The quantity of natural resin thus obtained from a pale mineral oil should not, says Holde, exceed 0·3 per cent., and from a dark oil 1·0 per cent. If a quantity notably in excess of these be obtained, the treatment with 70 per cent. alcohol should be repeated until the whole of the resin has been extracted, and after weighing the residue it should be tested by the Liebermann-Morawski reaction in order to ascertain whether colophony has been added to the oil. The addition of colophony would, however, raise the acidity of the oil, 1 per cent. of acidity as oleic acid being equivalent to about 1·24 per cent of colophony. If, therefore, the acidity of a mineral oil (determined as described on p. 207) be less than 0·1 per cent., not more than 0·12 per cent. of colophony can be present.

(*b*) *Detection and Estimation of Asphalt.*—About 0·5 c.c. of the oil is shaken in a test-tube or small flask with 40–50 c.c. of petroleum spirit boiling below 35° C., and allowed to stand. In the presence of asphalt, dark insoluble flakes appear, either immediately or within 24 hours, which, when collected on a filter, resemble asphalt in appearance and, whilst freshly precipitated, dissolve completely in coal-tar benzene.

To estimate the amount, from 1·5 to 3 grms. of an oil rich in asphalt, or from 5 to 20 grms. of an oil poor in asphalt, are dissolved in from 300 to 500 c.c. of petroleum spirit and allowed to stand for at least 24 hours, when the greater part of the precipitate will have settled. The clear liquid is then

[illegible]

[illegible]

[illegible]

[illegible] tested in a Martens machine, the coefficient of friction was found to be so high, and the rise of temperature of the bearing so rapid as to condemn the oil as a lubricant. By dissolving the oil in a mixture of alcohol, 3 parts, and ether, 4 parts, the caoutchouc was left insoluble, and the amount present was estimated by collecting the insoluble flakes, washing, drying, and weighing them.

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* If allowed to stand, the precipitate is apt to become less soluble in benzene.

† *Die Untersuchung der Schmiermittel*, p. 122.

W.—DETECTION OF SOAP AND INORGANIC SUBSTANCES IN MINERAL OILS AND GREASES.

For the detection of soap in lubricants, about 0·5 c.c. of the sample is shaken with 5–10 c.c. of petroleum spirit (redistilled below 75° C.), until dissolved or thoroughly disintegrated. Two cases then present themselves:—

(α) *A clear solution is obtained.*—Add 1 c.c. of Schweitzer and Lungwitz's reagent (a saturated solution of metaphosphoric acid in absolute alcohol, made by shaking excess of the powdered acid with alcohol in a stoppered bottle).* If soap be present, even in traces, a flocculent precipitate will be produced.

This test was specially devised for the detection of the small quantities of aluminium soap ('viscom,' 'gelatin') which are sometimes added to mineral oils to produce a factitious viscosity. The reaction depends upon the fact that whilst free metaphosphoric acid is soluble in alcohol and in ether, aluminium metaphosphate and the metaphosphates of the alkalies and alkaline earths are insoluble. The authors of the test have proved by experiments with a large number of fixed oils and fats, mineral oils, rosin oil, vaseline, etc., that if no soap be present no precipitate is obtained in 24 hours. Some waxes, however, also ozokerit, are precipitated from their solutions in petroleum spirit by absolute alcohol; therefore, if pure absolute alcohol (free from phosphoric acid) be found to give a precipitate, the test must be repeated, using ordinary ether as the solvent and a solution of metaphosphoric acid in ether as the reagent.

(β) *An insoluble residue remains.*—Dissolve, if necessary, a larger quantity of the substance in more petroleum spirit, filter through a small filter paper, and wash with petroleum spirit until all soluble oily matter is removed. Then drive off the petroleum spirit by evaporation, transfer some of the dry residue to a small test tube, and heat it with dilute hydrochloric acid. Soap, if present, will be decomposed, and the fatty acids set free will be seen floating on the liquid, either while hot or after cooling. If the result be uncertain, shake the cold liquid with a little ether, draw off the ether with a pipette, and evaporate it in a watch glass to detect the fatty acid, which will crystallize on solidification. Resin would be recognized by its physical characters. The base of the soap, whether aluminium, calcium, sodium, lead, etc., may be detected by pouring the acid solution through a wet filter and applying the usual tests.

Another portion of the residue insoluble in petroleum spirit may be burnt in a small platinum dish or porcelain crucible. If no ash remain, the insoluble matter was free from soap. If soap be present, an ash consisting of the carbonate or oxide of the metallic base will be obtained.

The residue insoluble in petroleum spirit may contain, besides soap, other substances, such as graphite, soapstone, chalk, lime, barytes, starch, etc.

Graphite would be recognized by its blackness and lustre. It would be difficult to burn, requiring a high temperature or a stream of oxygen. *Soapstone* and *barytes* would not dissolve in dilute hydrochloric acid, and could be filtered off and identified by the usual qualitative tests. *Free lime* would give a red colour with phenolphthalein; *chalk* would not, but would effervesce on adding acid. *Starch* would be detected by the blue colour with iodine.

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* *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 1178.

X.—DETERMINATION OF ASH.

The ash of any oil or fat free from water may be determined by weighing 10 grms. in a tared platinum dish, placing the dish at the mouth of a Fletcher's gas muffle heated to dull redness, and, as soon as the oil begins to smoke, igniting it with a match. The dish is then placed in such a position that the oil will burn quietly away, most of the smoke being drawn into the muffle (which is perforated at the back). When nothing but a charred mass remains, the dish is placed inside the muffle until the carbon is completely burnt off, then carefully removed to a desiccator to cool, and weighed. The particles of ash are often very light, and may easily be carried away by currents of air.

In 22 samples of pure mineral oil examined by Archbutt, mostly dark-coloured machinery oils for railway work, the percentages of ash were:—*maximum*, 0·055; *minimum*, 0·002; *average*, 0·015. In 36 samples of dark cylinder oil, the following percentages were found:—*maximum*, 0·080; *minimum*, 0·002; *average*, 0·025. These ashes were generally red in colour, and probably consisted largely of oxide of iron from the still. Pale, refined, mineral oils may be expected to leave much less ash than the majority of these samples. If a high ash be found in a pale mineral oil, an aluminium soap ('viscom,' 'gelatin') may have been added to produce a factitious viscosity; in that case the ash will consist chiefly of alumina.

Pure fatty oils and fats leave mere traces of ash, bone fat, which contains lime, being an exception.

Soap-thickened greases which contain water, should first be heated over a very small flame and stirred with a platinum rod until all the water has evaporated. The dish, and the rod which should have been weighed with it, are then placed in the mouth of the muffle and treated as above directed. In the presence of soap, more or less considerable quantities of ash will be obtained, consisting of calcium or sodium carbonates, etc., etc., according to the nature of the soap.

Y.—DETECTION OF NITROBENZENE AND NITRONAPHTHALENE.

These compounds are used for the purpose of disguising the presence of mineral oils, by destroying their fluorescence or 'bloom.' Nitrobenzene is easily recognizable by its powerful and characteristic odour of oil of bitter almonds, but nitronaphthalene cannot be detected by its smell. Greases are frequently scented with nitrobenzene to disguise the nature of the fat or oil used in their preparation. For the detection of nitronaphthalene, the following test, depending upon its reduction to naphthylamine, has been proposed by Leonard* and by Holde.†

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* *Chem. News*, lxviii. (1893), p. 297.

† *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 906.

A few cubic centimetres of the oil are warmed in an Erlenmeyer flask with zinc dust and dilute hydrochloric acid, and the mixture is frequently agitated. During this process, the fæcal odour characteristic of α-naphthylamine will be perceived. After the reduction is complete, the contents of the flask are poured into a separating funnel, and the acid liquid is drawn off through a filter paper into another separating funnel. It is there treated with sufficient caustic soda solution to redissolve the zinc hydrate at first precipitated and, after cooling, is shaken with ether, which dissolves the liberated α-naphthylamine, the presence of which is indicated by the violet colour and fluorescence of the ethereal solution. The latter, after drawing off the aqueous liquid and washing with water, is evaporated to dryness, leaving a residue of the violet-coloured base. On treating this residue with a few drops of hydrochloric acid, the chloride is formed, which remains partly insoluble and partly soluble, but, on evaporating the excess of acid and adding water, a clear aqueous solution is obtained, in which ferric chloride gives an azure blue precipitate. When filtered, this precipitate becomes purple-red, and the filtrate blue-violet. Instead of treating the residue with hydrochloric acid and testing with ferric chloride, it may be dissolved in a little alcohol. On then adding a drop of a solution of sodium nitrite acidified with acetic acid, a yellow colour is produced, which is changed to crimson by hydrochloric acid.

Nitrobenzene, if present, is reduced by the zinc dust and hydrochloric acid to aniline, which is obtained on evaporating the ethereal solution as described above, either pure or mixed with α-naphthylamine, according to whether nitronaphthalene were simultaneously present or not. On treatment with hydrochloric acid, pure aniline dissolves readily, and on diluting and adding ferric chloride a green precipitate is produced, which afterwards turns deep blue, and does not become purple-red even on long standing; the filtrate, instead of being blue-violet, is yellow. When α-naphthylamine and aniline are present together, the precipitate is at first azure blue, afterwards dirty red-brown, and finally purple-red, and the filtrate is violet.

Z.—DETECTION AND ESTIMATION OF WATER.

The presence of water in pale oils is indicated by the appearance of turbidity, or by actual visible drops of water which sink in the oil instead of rising as air-bubbles do. Water in greases is indicated by the frothing and crackling which occurs when a small quantity of the grease is heated in a dry test-tube, and by the condensation of drops of water on the upper, cool part of the tube; whilst the grease, if free from water, will melt quietly to a clear fluid. A more delicate test for the presence of traces of water in oils (especially dark oils) is recommended by Holde. A small quantity (3 or 4 c.c.) of the oil is placed in a small dry test-tube, the interior of which is first coated all over with a film of the oil. The end of the tube containing the oil is then heated by being immersed just below the surface of a paraffin bath at 160°–180° C., when, if the sample contains water, the vapour will condense on the cool, oily, inner surface of the tube, above the level of the oil, forming a visible, cloudy emulsion.

The estimation of water in lubricating greases may be made by one of the following methods:—

1. *By heating in an air-bath at* 105°–110° *C.*—About 5–10 grms. of the well-mixed grease are placed in a small tared beaker, and the exact weight is taken. The beaker is then heated in the air-bath at 105°–110° C. until frothing has ceased and the grease has melted down to a clear oil free from visible drops of water. It is then cooled and re-weighed.

2. *By stirring with a thermometer over a naked flame.*—100 grms. of the grease are heated in a weighed porcelain basin over a small flame, and continually stirred with a thermometer at a temperature not exceeding 105° C. (221° F.) until frothing has ceased and the grease is in calm fusion. The basin and contents, when cold, are re-weighed. If the thermometer bulb is well drained into the basin while hot, the small quantity of adhering fat may be neglected; or, the bulb may be wiped with a small piece of filter paper which was counterpoised with the basin.

CHAPTER VIII.

THE SYSTEMATIC TESTING OF LUBRICANTS BY PHYSICAL AND CHEMICAL METHODS.

The analytical examination of lubricants is conducted with different objects and on different lines according to the nature of the sample to be tested. If this be an undescribed oil, the primary object is to ascertain whether the substance is a hydrocarbon oil free from fatty oil, a fixed oil or fat free from hydrocarbon oil, or a mixture. An undescribed hydrocarbon oil may be a mineral oil from petroleum or shale, a rosin oil, a coal-tar oil, or a mixture of these. A mineral oil is subjected chiefly to physical tests to ascertain its viscosity, flashing-point, etc., in order to determine whether it is suitable for use as a spindle oil, a machine or engine oil, or a cylinder oil; and to such chemical tests, in addition, as will shew whether the oil has been sufficiently refined, and is free from acidity and from rosin and coal-tar oils. A fixed oil, such as rape oil, olive oil or tallow, is tested first of all to ascertain whether it is sufficiently free from acidity (see p. 208), and then more elaborately to prove whether the sample is genuine or adulterated, and especially whether any oil of drying or semi-drying character has been added which would tend to increase the natural tendency of the oil to thicken or gum by oxidation. A mixed lubricant (which includes most greases) containing both hydrocarbon oil and fixed oil, in addition perhaps to soap, water, etc., is first tested qualitatively to find out the nature of the main ingredients, and then a more or less complete quantitative analysis is made with the object of ascertaining the composition of the mixture. The information thus obtained may be supplemented by viscosity and other tests, as in the case of a pure mineral oil.

A.—UNDESCRIBED OILS.

The nature of an undescribed lubricating oil, if simple and not a mixture, is almost always indicated by the smell, taste, or appearance (colour, fluorescence, consistency, etc.). How much can be determined in this way in the case of a mixed oil depends upon the experience

[illegible]

[illegible] spindle oils and some engine [illegible] cylinder oils).

For the sake of uniformity, the colour and appearance should be observed under standard conditions, *e.g.*, in a ¼-inch (Lovibond) glass cell with parallel flat sides, held first between the eye and a window (appearance by transmitted light) and then with the observer's back to the window (appearance by reflected light). Fluorescence may be observed by looking down into the cell held below the edge of a table or bench fronting a window. Redwood examines pale-coloured oils by means of Lovibond's tintometer, using a 2-inch cell and matching the colour by means of coloured glasses.* For a description of Lovibond's tintometer, see *Jour. Soc. Chem. Ind.*, ix. (1890), p. 10.

Mineral lubricating oils should not have any empyreumatic odour.

Specific Gravity.—This is determined by one of the methods described in Chapter VI. section B (p. 164), and little need be added to what has there been said. The bottle method is most suitable for the thicker oils, but the Westphal balance may be used for spindle oils and the lighter machine oils. The specific gravity is of little importance in regard to the lubricating value of an oil, but it serves to identify the particular oil required, and in some measure to detect the presence of rosin and tar oils. The specific gravities of mineral lubricating oils are given in the table on p. 177.

Viscosity.—This is the most important property of a mineral oil which can be measured in the laboratory. The knowledge of it determines whether an oil is suitable for use as a spindle oil, an axle oil, a machine or engine oil, or a cylinder oil. The determination is usually made at two temperatures, viz., at 60° or 70° F. if the oil be fluid at those temperatures, and, in the case of spindle and machine oils, also at 100° or 140° F. In order to ascertain the extent to which the viscosity is affected by rise of temperature, cylinder oils are conveniently tested at 100° and 212° F.; there is not much to be gained by going higher, though in Redwood's viscometer a determination can be made at as high a temperature as 400° F. The determination should be made either by Redwood's viscometer (p. 138) or by Coleman's (p. 140); the latter is most convenient for temperatures up to 212° F. All results should be expressed, if possible, in absolute measure (p. 147) as well as in terms of rape or other known oil. The viscosity of a number of oils, in dynes per sq. cm., are given in the table on p. 159. Table XC. (p. 298) will enable an oil to be roughly classified.

Flashing-Point and Volatility.—The flashing-point, determined by the Pensky or Gray testers (pp. 178–182), should not be lower than 300° F. for out-door machinery and 340° F. for mill work. Cylinder oils should flash at temperatures well above that of the cylinder in which they are intended to be used, say at from 450° F. to 600° F. All cylinder oils should be tested for volatility by Archbutt's method (p. 183) and should not lose more than 1 per cent. in 1 hour at the mean cylinder temperature. Machine oils flashing below 300° F. should also be tested for volatility at 100° F. and 200° F., the test were continued until the oil ceases to lose more than 0·5 per cent. in [illegible]. A good lubricating oil should lose little or nothing at these temperatures. A natural mineral oil flashing at 200°–210° F. was

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* *Petroleum*, vol. ii. p. 596.

TABLE [illegible].—VISCOSITIES IN DYNES PER SQ. CM.

[illegible] Viscosities of Mineral Lubricating Oils.			Purposes for which the Oil is used.
[illegible]	[illegible]	[illegible]	
[illegible] [illegible] [illegible]	[illegible] [illegible] [illegible]	..	For spindles and light high-speed machinery: usually mixed with animal or vegetable oil.
[illegible] [illegible]	[illegible] [illegible] [illegible]	..	For spindles, pure, or with very slight admixture. For light machine tools, lathes, printing machines, looms, shafting, etc.: usually mixed. For marine engines and heavy work if mixed with 'blown' oil.
[illegible] [illegible]	[illegible] [illegible] [illegible]	..	For engines, pure or mixed.
[illegible] [illegible] [illegible]	[illegible] [illegible] [illegible]	[illegible]	For railway car and tram-car axles, pure or mixed, according to viscosity.
[illegible] [illegible]	[illegible] [illegible] [illegible]	[illegible]	For locomotive engines, usually mixed with rape oil.
	[illegible] [illegible] [illegible]	[illegible] [illegible] [illegible]	For cylinders and very heavy machinery. For the lighter high-speed engines and machinery in hot situations. Used either pure or mixed.
[illegible]			Description of Oil.
[illegible]	[illegible]	[illegible]	Sperm oil.
[illegible]	[illegible]	[illegible]	Olive oil.
[illegible]	[illegible]	[illegible]	Rape oil.
[illegible]	...	[illegible]	Tallow.
[illegible]	2·73	0·17	Castor oil.

found to lose 6 per cent. by evaporation at 100° F. and 17 per cent. at 2[illegible]0° F.

Setting-Point or Cold Test—This, in the case of oils (not greases), should obviously be as much as possible below the temperature at which the oil is to be applied. The test is, of course, most important in the case of oils for out-door machinery, such as railroad oils. For such purposes, summer oil should remain fluid at 32° F., and winter oil at 15° F., if possible, but allowance must be made for American oils, which will not, as a rule, withstand so low a test. (See table on p. 192.)

General Purity and Freedom from Adulteration.—In addition to the foregoing, there are certain tests as to which circumstances must decide whether they should be made or not; these are for the detection of impurities, unacknowledged additions, or adulterants. The chief of such substances to be looked for in mineral oils are—

(*a*) *Soap.*—Every mineral oil which has a non-homogeneous appearance, or an unnatural viscosity, or which exhibits a tendency to form threads in dropping should be tested for soap by the methods described in Chapter VII. section W (p. 291). If soap be found, its nature can be ascertained by the analysis of the ash (see p. 292; also section E, p. 317). By well shaking some of the soap-thickened oil with dilute hydrochloric in a stoppered bottle heated by immersion in hot water, then pouring the contents into a separating funnel, drawing off the acid, and well washing the oil with hot water, the mineral oil can be obtained in its natural state and its true viscosity determined.

(*b*) *Ash.*—Every mineral oil leaves some ash when burnt, but the quantity is usually minute (see p. 292). In an oil the origin of which is unknown, the amount of ash should always be determined. An abnormally high ash indicates either the presence of soap or imperfect refining.

(*c*) *Fixed Oil or Fat.*—An oil sold as a pure mineral oil and at a low price is not likely to contain a fixed oil; but special brands of mineral oil, especially cylinder oil, not unfrequently do contain an unacknowledged small quantity of animal or vegetable oil to which some good or bad quality, revealed in practice, may be due. Therefore, in testing an unknown oil alleged to be purely mineral, it is always desirable, sometimes most necessary, to prove the absence of fat by careful chemical analysis. For this purpose Ruhemann's test may be used (p. 209), but the quantitative method described on p. 224 is the only absolutely certain test.

(*d*) *Acidity.*—Any refined mineral oil containing more than 0·2 per cent. of total acidity calculated as oleic acid should be tested for free mineral acid (usually sulphuric). The method is described on p. 208. It is seldom necessary to test natural and reduced oils. Abnormally high acidity may, of course, be due to the presence of resin acids contained in rosin oil added as an adulterant; therefore, time might be saved by testing for rosin oil before testing for mineral acid. Resin acids can, if desired, be isolated by the method described on p. 227.

(*e*) ***Rosin Oil.***—The methods of detecting and estimating the proportion of this adulterant are described at pp. 282–287.

(*f*) *Gumming Property.*—This is not a property of pure mineral oils, as such oils do not gum, at any rate not by oxidation like the fixed oils. The remarks under this head on pp. 261–265 should be read, where the causes which may lead to the formation of deposits by mineral oils are discussed. If there be any reason for investigating the tendency to form a gummy or sticky residue which a pure mineral oil may appear to exhibit in practice, the 'film-test' described on p. 255 may be used. In some cases it may be desirable to make such a test upon a surface of steel or other metal, or upon a painted surface.

(*g*) *Asphalt and Tar.*—Little need be added to what has been said in Chapter VII. section U (p. 288), except that the special tests for these bodies are seldom necessary in the case of Russian and American oils, and need only be made if the practical results indicate their presence in an objectionable degree.

(*h*) *Caoutchouc.*—According to Archbutt's experience, this is a rare admixture. If, however, stickiness or unnatural viscosity of a mineral oil be found, notwithstanding the absence of soap, then caoutchouc should be searched for. See p. 290.

(*i*) *Mechanical Impurities.*—Grit and dirt in a mineral oil would be detected by straining the oil through fine wire gauze or muslin. Water is detected by the tests described in section Z (p. 293).

C.—FIXED OILS AND FATS.

The most important and useful physical and chemical data for the recognition of the lubricating oils belonging to this class are included in the table on pp. 302–3, and in the following pages hints for the examination of each oil are given.

The first test to make in examining any fixed oil intended for lubrication is the determination of *acidity*. This is especially important in the case of olive oil, tallow, palm oil (and coconut oil). The two last, as commercially met with, are usually quite unfit for lubrication. The more delicate and intricate the machinery the greater the need for selecting the least acid oil, and the smaller the maximum of acidity permissible; for no machinery should oil be used containing more than 4 per cent. of free (oleic) acid. The reason for this statement and the methods of determining acidity will be found in Chapter VII. section A (p. 201).

Wool or cloth oils are not here alluded to. They often contain very large amounts of free fatty acids; indeed, commercial oleic acid is used as a wool oil under the name of 'oleine'; such oils are quite unsuitable for the lubrication of machinery. According to Mackey, free fatty acids in wool oils greatly increase the risk of fire (see p. 268).

Rape Oil.

Refined rape oil for lubrication and burning should be clear, and pale yellow in colour.

The **total acidity**, calculated as oleic acid, should not exceed 4 per cent. Of 230 samples of commercial refined rape oil examined by Archbutt, 84 per cent. satisfied this condition (see p. 202). Low acidity is of great importance if the oil be required for burning in lamps, since free fatty acids as well as free mineral acid have a charring action upon the wick.

In rape oil refined by sulphuric acid, traces of free sulphuric acid exist, as is proved by the following experiments.

100 c.c. of rape oil and 100 c.c. of distilled water were placed in a large beaker on a steam-bath, and steam was blown through the mixture vigorously for half an hour. The oil and water were then poured into a separating funnel, the water was drawn off through a wet filter paper, and the oil was washed with a little more water. After concentrating the aqueous liquid to rather less than 50 c.c. it was again filtered, and the filtrate was titrated with decinormal soda, using methyl orange as indicator. The following results were obtained :—

Oil refined at	Sulphuric Acid (H_2SO_4) per cent.
Stettin, ...	0·0056
Hull, 1st sample, ...	0·0050
Hull, 2nd sample, ...	0·0026

The neutralized liquids were boiled down to 2–3 c.c. and tested with barium chloride, and in each case a precipitate of barium sulphate was obtained which was estimated by the eye to about correspond with the result obtained by titration. These samples being commercial oils of good quality, not selected, it may be assumed that the percentage of *free mineral acid* in refined rape oil should not exceed 0·006 per cent. of H_2SO_4, which is equivalent to 0.035 per cent of oleic acid.

The **specific gravity** of refined rape oil at 60° F. should be 0·914–0·9155; it should not exceed 0·9160, and if above 0·9165 either ravison or other oil of more strongly drying character than rape is probably present. A lower sp. gr. than 0·914 would be suspicious, for, although perfectly genuine rape oil may be as low as 0·9132 in sp. gr., such oil is seldom met with in this country. An abnormally low sp. gr. might be due to adulteration with light mineral oil.

The **viscosity** of rape oil is exceptionally high, and is a very valuable indication of its purity. All fixed oils likely to be added as adulterants would lower the viscosity, and although this could be counteracted by adding castor oil or blown oil, the presence of these

TABLE XCI.—VEGETABLE AND A

Reference to complete Tables, page	Physical and Chemical Constants.	Rape Oil (Colza Oil).	Olive Oil.	Castor Oil.	Palm
176	Specific gravity at 60° F.,	0·9140–0·9165	0·914–0·917	0·961–0·968	0·92
159	Viscosity (dynes per sq. cm.),	1·09–1·16 at 60° F.	1·00 at 60° F.	2·73 at 100° F.	..
191	Setting-point, ° F.,	11–28	21–39	−0·4 to +14	..
196	Melting-point, ° F.	..	..	..	50- when fre excess o
199	Refractometer value at 22° C.,	+15° to +20°	0° to +3·5°	+37° to +46°	..
213	Saponification value, %,	17·0–17·5	18·5–19·6	17·6–18·7	19·6-
228	Hehner value, %,	95·0–95·1	94–96	95·3–95·5	94·2-
232	Reichert value; c.c. per 2·5 grms.,	..	..	..	..
232	Reichert-Meissl value; c.c. per 5 grms.,	0·4–0·9	0·45–1·5	2·2–4·0	0·
237 239	Acetyl value, %,	0·79	1·35–1·36	15·0–15·5	..
245	Iodine value, %,	97·5–106	76–89 (usually 81–85)	83·5–86·5	51-
252	Maumené thermal value; 50 grms. oil, 10 c.c. of 97 % sulphuric acid, ° C.,	58–64	40–45	56–66	..
223	Unsaponifiable matter, %,	0·6–1·5	0·8–1·5	0·3–0·8	1
	Mixed Fatty Acids.				
177	Specific gravity at $\frac{100°}{100°}$ C.,	0·875–0·876	0·874–0·876	..	0·
197	Solidifying-point or titre-test, ° C.,	12·2–18·5	17·2–26·4	..	35·9-
197	Melting-point, ° C.,	16–21	19–28·5	13	41-
245	Iodine value, %,	96·5–105·5	86–90	86·5–88·5	5
	Mixed Alcohols.				
177	Specific gravity at $\frac{100°}{100°}$ C.,	..	..	..	..
221	Melting-point, ° C.,	..	..	..	..
246	Iodine value, %,	..	..	..	..
234	Saponification value of Mixed Acetates, %,	..	..	..	..

OR LUBRICATION.

	Tallow (Beef and Mutton).	Tallow Oil. (Ox Oil.) (Animal Oil.)	Lard Oil.	Neatsfoot Oil.	Whale Oil.	Sperm Oils.		Porpois and Blackfis Jaw Oil
						Southern.	Arctic.	
	0·937–0·953	0·916–0·919	0·913–0·919	0·915–0·918	0·921–0·923	0·875–0·884	0·879–0·881	..
	0·18 at 150° F.	1·04–1·13 at 60° F.	0·99 at 60° F.	about same as tallow oil	..	0·39–0·42 at 60° F.		..
	..	variable, say 32–46	25–42 (occasionally lower)	..	..	about 32		..
	108–124	..	..	..	..	..		..
	..	..	0° to +1°	-1° to -4°	30·5° to 48°	-12° to -17°		..
·8	19·0–19·8	19·3–20·0	19·42–19·53	19·4–19·8	18·8–19·4	12·0–14·7	12·3–13·6	25·4–29·
·5	95–96	..	..	95·3–95·5	93·5	..	..	66·3–72·
	..	..	..	..	0·7–12·5	1·3	1·4	47·8–65·
·5	1·0–1·2	..	..	..	..	..	..	131·6
	0·98	..	..	..	..	..	..	..
·5	32·7–46·2	55–60	60–82 (according to setting-point)	69–75	120–130	81·3–84·4	80·4–82·1	31–50
	..	40–43	41–46	(40–46?)	85–92 (?)	45–51	42–47	..
	0·5	..	..	..	0·65–3·72	37·4–41·5	31·7 (?)–39·7	..
	0·870	..	..	0·874–0·880	..	..	..	..
25·2	33·3–48·3	..	..	26–27 (sheep's foot oil 21–22; horse's foot oil 28·6)	..	11·1–11·9	8·3–8·6	
-27	42–54	..	..	..	..	13·3	10·3–10·8	
-9·5	26–41·5	..	..	..	..	83·2–88·1	82·2–83·3	
	..	..	..	..	..	0·8271	..	
	..	..	..	..	..	23·5–27·5		
	..	..	..	..	..	67·9	69·3	
	..	..	..	..	..	18·49	18·62	

* Neutral oil prepared in the laboratory from commercial oil.

oils would be indicated by other abnormal characters, castor oil raising the acetyl value and both oils raising the specific gravity. Rosin oil or heavy mineral oil, if present, would be detected in the unsaponifiable matter.

The **saponification value** of genuine rape oil ranges from 17·00 to 17·50 per cent. This statement is based upon the examination of hundreds of samples of the commercial oil tested by Archbutt during the past 18 years. A value in excess of 17·50 is probably due to the presence of ravison or other more strongly drying oil. On the other hand, a value lower than 17·0 would indicate the presence of an unsaponifiable oil, or possibly of sperm or bottlenose oil. The test must, of course, be made with every precaution to ensure accuracy, otherwise the limits cannot be so strictly defined.

The **Maumené value**, or rise of temperature on mixing 50 grms. of the oil with 10 c.c. of sulphuric acid (97 per cent. H_2SO_4), ranges from about 58° C. to 64° C.; the result depends to some extent upon the 'personal equation' of the operator, which is not serious if the instructions given on p. 251 are strictly adhered to. A high result indicates the presence of ravison or other drying or semi-drying oil, and a low result indicates mineral or sperm oil.

The **unsaponifiable matter**, determined by the method on p. 215, should not exceed 2 per cent. in genuine commercial rape oil. In the expressed oil it is below 1 per cent., but in the oil extracted from the seed by petroleum spirit 1 per cent. must be allowed for residual hydrocarbons. If a larger proportion than 2 per cent. be obtained, it should be purified by re-saponification as directed on p. 223, and if still materially in excess of 2 per cent., the product should be examined as directed in Chapter VII. section F (p. 219), to ascertain whether hydrocarbons (mineral or rosin oil), cholesterol (from animal oils), or wax alcohols (from sperm or bottlenose oils) are present. In genuine rape oil the unsaponifiable matter consists very largely of phytosterol, which may be obtained in characteristic tufts of needle-shaped crystals by dissolving the unsaponifiable matter in 2–3 c.c. of warm 90 per cent. alcohol and cooling the solution.

Rape oil should always be subjected to the **oxidation test** described on p. 255 (watch-glass test), a standard sample of known purity being tested at the same time and under the same conditions.

Halphen's **colour reaction** for cottonseed oil (p. 280) and the furfurol test for sesamé oil (p. 281) should not be omitted; both are very delicate, and the result must be interpreted in accordance with the quantitative values. According to Archbutt's experience, these reactions may be relied upon to give negative results with genuine rape oil. If a red colour be obtained by Halphen's test, the presence of cottonseed oil should be confirmed by the Milliau test (p. 278), using the fatty acids which may be easily obtained from the soap solution left after isolating the unsaponifiable matter. Some genuine rape oils have a slight, slow reducing action on the silver solution; but an immediate, decided reduction proves the presence of cottonseed oil, of reduction is usually in proportion to the percentage present.

amed tests suffice for the detection of the usual :—*ravison, cottonseed, maize, linseed, and the drying nal oil, and Arctic Sperm oil.* The latter, though pensive than rape oil, is sometimes added in order to he gravity and saponification values which have been ration with oil such as cottonseed.

ementary test, the **iodine value** is useful for confirming of ravison oil, maize oil, the drying oils, and some fish ave higher iodine values than genuine rape oil. It is of e detection of cottonseed oil. These oils (except cotton- he solidifying and melting points of the mixed fatty acids. tty acids of genuine rape oil solidify at 10·5° to 18·5° C., s from ravison oil do not solidify at 0° C.

Olive Oil.

utral olive oil is one of the finest lubricants we possess, but tely, a great deal of it is spoiled previous to extraction, by he pulp to ferment and the oil to become decomposed (see nd 202); also by storing the oil in a crude state. Olive oil for lubrication must therefore be carefully examined for p. 207). 4 per cent. of free oleic acid should be the maximum by large consumers; small quantities of oil intended for the ion of delicate machinery may be purified from every trace by refining with soda (see p. 209).

e oil should be clear, and pure yellow or greenish-yellow in Some perfectly genuine olive oils are green or brownish- the colour being due to chlorophyll, which may be identified by of its characteristic absorption bands if the oil be submitted to scopic examination. But there are some adulterated oils which ificially coloured green by *copper*; this may be detected by g some of the oil with ether and shaking with dilute sulphuric hich will remove the green colour. On drawing off the acid and adding excess of ammonia, the deep blue colour character- cuprammonium will be obtained.

e oil, being one of the most expensive lubricating oils, is very to adulteration. The most valuable instrument for the rapid on of adulteration is the **oleo-refractometer** (see p. 198). As seen by reference to the table on p. 199, the recorded deviation by genuine olive oil ranges from 0° to +3·5°. 106 samples ed by Oliveri* ranged from 0° to only 1·2°. All fixed oils to be added as adulterants would increase the refraction, except eatsfoot, and tallow oils. Arachis oil, which has a deviation y +3·5 to +7·0, would not be detected unless present in large tion, but would be found by **Renard's test** (p. 273).

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* *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 45.

[illegible] specific gravity of [illegible] olive oil at 60° F. usually [illegible] may rise to 0·919 in [illegible] the oil from the kernel [illegible] for lubricating without [illegible] to oxidise and gum. [illegible] F. on a watch-glass [illegible] the same weight of a sample of known [illegible] specific gravity should be subjected [illegible] examination for adulterants, [illegible] oils. Adulteration [illegible] by the specific gravity.

[illegible] value [illegible] usually ranges from about [illegible]. Some oils are met with having a [illegible]. This was the [illegible] iodine value [illegible] which was found to possess a [illegible] F., saponification value [illegible] the unsaponifiable matter amounted [illegible] and the colour reactions [illegible] were quite negative. The acidity was [illegible] appeared to be due to an excess [illegible] and depositing a [illegible] at a temperature of 45° to 47° F. A few [illegible] of which had an iodine [illegible] per [illegible] for [illegible] California olive oil [illegible] white mustard [illegible]. This [illegible] and would at the same time lower the [illegible]

[illegible] saponification value of [illegible] oil, according to [illegible] samples, may range from 185 to [illegible] agrees that it is [illegible] samples of commercial olive oil examined [illegible] as low as 18[illegible] this from its colour [illegible] kernel [illegible] the values of the other samples ranged [illegible] per cent. A low saponification value might be [illegible] olive-kernel oil, which can scarcely be regarded [illegible] adulteration with rape, mustard, Arctic [illegible] oil. No adulterant likely to be added would materially [illegible] the saponification value of olive oil.

[illegible] possible that lard oil was present in these samples. Lard oil is [illegible] worth while to prove its presence, the method would be [illegible] the stearin which is absent from pure olive oil. Hehner and Mitchell, [illegible] — Lewkowitsch, *Analysis of Oils*, etc., p. 455. [illegible], vol. i., p. 457.

The **Maumené value** of genuine olive oil, determined as directed on p. 251, is lower than that of any other vegetable oil, ranging, according to our experience, from 40° to 45° C.; this test is, therefore, of great value for the detection of adulteration.

The **unsaponifiable matter** in genuine olive oil does not exceed 1·5 per cent.; a higher result than this would probably be due to the presence of hydrocarbon (mineral or rosin) oil, or of wax alcohols from Arctic sperm oil.

With reference to specific adulterants, the following remarks may be made:—

Cottonseed oil, unless it has been heated, is detected with certainty by Halphen's test (p. 280) or by the Milliau test (p. 278), both of which give negative results with pure olive oil and are sufficiently delicate to detect as little as 2 per cent. of cottonseed oil, if present. Olive oil adulterated with cottonseed oil would, of course, contain more than this percentage, and the presence of the foreign oil would be confirmed by the increased refractive power, iodine value and Maumené value of the sample, also by the result of the oxidation test; without this confirmation of the colour reactions, the presence of cottonseed oil as an adulterant could not be certified.

Sesamé oil is detected, with certainty, by the very delicate Badouin reaction (p. 280). Some genuine olive oils give a rose coloration, but it is unlikely for error to occur if the sample be submitted to confirmatory quantitative tests. Sesamé oil, if present as an adulterant in olive oil, would raise the refractive power, iodine value, and Maumené value of the oil, and would increase its drying and gumming property.

Earthnut (Arachis) oil can only be detected in olive oil by Renard's process, although the presence of the oil might possibly be indicated by an abnormally high iodine value. Earthnut oil of the best quality is a non-drying oil, and if a sample of olive oil containing this oil be found to possess no undue tendency to oxidize, there is only the substitution of a cheap oil for one of greater value to be objected to. Some earthnut oils are not 'non-drying,' and olive oil containing such is spoiled for lubrication. It must not be forgotten that rape, mustard, and perhaps other oils from cruciferous plants contain arachidic acid. These oils would betray their presence by lowering the saponification value, and by raising the iodine and Maumené values, of olive oil.

Castor oil would raise the specific gravity, viscosity, and acetyl value of the sample, besides increasing the solubility of the oil in alcohol.

Curcas oil would raise the specific gravity and the Maumené and iodine values, and would increase the tendency to oxidize.

Arctic sperm oil, also *mineral and rosin oils*, would betray their presence by increasing the percentage of unsaponifiable matter, and could be identified with certainty and the amount estimated by examining the latter.

Lard and tallow oils would be the most difficult to detect. They would probably raise the setting-point; but, being non-drying oils and good lubricants, their presence would not necessarily be objectionable, except for the fraud. (See note at bottom of page 306.)

Castor Oil.

Castor oil for lubricating should be clear, pale in colour, and as free as possible from acidity.

For the detection of **adulterants**, advantage may be taken of the easy **solubility** of the genuine oil **in alcohol**. Absolute alcohol dissolves castor oil in every proportion: 90 per cent. alcohol (sp. gr. 0·834) dissolves less, 1 volume of castor oil requiring from 2·4 to 2·94 volumes of 90 per cent. alcohol at 20° C. according to experiments by Italie.[*] A sample of genuine castor oil tested by Archbutt was perfectly soluble in 2 volumes of 90 per cent. alcohol at 15° C. Twenty-three samples of Indian castor oil, examined by Deering and Redwood, were completely soluble in 3 volumes of alcohol of sp. gr. 0·830 at 60° F. (15·5° C.). It appears, therefore, that castor oil, if genuine, should dissolve completely in 3 volumes of 90 per cent. alcohol at 20°. It is usual, however, to employ 5 volumes of alcohol, as recommended in the *British Pharmacopœia* (1898), and we have found by experiment, with the sample of easily soluble castor oil referred to above, that when only 5 per cent. of either rape, blown rape, cottonseed, poppy, maize, or curcas oils were mixed with it, 5 volumes of 90 per cent. alcohol gave a strongly turbid mixture at 15° C., which deposited a small quantity of oil on standing. The following test, originally recommended by Finkener [†] (who used a slightly stronger alcohol), may therefore be employed with confidence as a rapid method of assay:—Measure exactly 10 c.c. of castor oil in a graduated, stoppered test cylinder, add 50 c.c. of alcohol (sp. gr. 0·834) and well mix. If genuine, a clear and bright solution will be obtained at 15° C. If as little as 5 per cent. of foreign oil be present, the liquid will remain strongly turbid even on warming to 20° C.

The **specific gravity** of castor oil should lie between 0·961 and 0·968, and is usually about 0·963–0·964. Adulteration with any other natural fixed oil or mixture of oils would lower the sp. gr., and although this might be adjusted by the addition of rosin oil (sp. gr. 0·96–1·00) the presence of the latter would be easily detected by determining the amount and examining the properties of the unsaponifiable matter, which, in genuine castor oil, does not exceed 1·0 per cent. Blown rape or blown cottonseed oil might be added without altering the density, and without causing any appreciable increase of the unsaponifiable matter.

The **viscosity** of castor oil greatly exceeds that of any other natural fixed oil, but it is exceeded by that of blown oil. Twenty-three samples of Indian castor oil, tested by Deering and Redwood in the Redwood viscometer, required from 1160 to 1190 seconds for the outflow of 50 c.c. at 100° F.

The **acetyl value** of castor oil (14·6 to 15·5 per cent.) exceeds that of any other known oil except grape seed oil (p. 237), and is one of the most valuable indications of its purity. Although blown oils also have a high acetyl value, they do not nearly approach castor oil in this respect (see p. 240), and the detection of 10 per cent. of blown oil is possible if the mixed fatty acids are thoroughly boiled with water to remove all soluble acids and then examined by Benedikt's process. Grape seed oil, if present in castor oil, would lower the specific gravity.

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[*] Lewkowitsch, *Analysis of Oils, etc.*, p. 421.

[†] *Jour. Soc. Chem. Ind.*, vi. (1887), p. 148.

The **Hehner value** (95·3 to 95·5 per cent.) would be lowered by adulteration with blown oil, as would also the iodine value (83·5 to 86·5 per cent.); on the other hand, the **Reichert-Meissl value** (2·2 to 4·0), the **Maumené thermal value** (56° to 66°), and the **saponification value** (17·6 to 18·7 per cent.) would be raised.

Among other possible adulterants mentioned by Allen, *poppyseed oil* would lower the specific gravity, acetyl value and viscosity, and would raise the iodine value; *lard oil* would lower the specific gravity, viscosity, acetyl and iodine values; *coconut oil* would lower the specific gravity and the Hehner and iodine values, and would raise the saponification value; and *seal oil* would lower the specific gravity, acetyl value and viscosity, and would raise the iodine value. *Cottonseed* and *sesamé oils* would be detected by the characteristic colour tests for these oils.

Palm Oil.

Palm oil is not as a rule adulterated with other fats, the chief impurities being free palmitic acid, dirt, and water. For grease-making, low acidity is of chief importance, as the dirt is strained off and the water settles out in melting. The **acidity** is estimated by the method described on p. 207, and should be neutralized by adding the necessary amount of soda in making the grease. The proportion of **dirt** and **water** can be determined roughly by melting the sample in a 100 c.c. cylinder standing in a beaker of hot water, and reading off the volume of sediment which is deposited. Anything under 2 per cent. may be neglected. If over 2 per cent., an allowance is usually made by the seller. In that case, a more accurate determination may be made by dissolving a weighed quantity of the well-mixed sample in ether, filtering, washing, evaporating the ether, drying the fat and weighing it; the difference between the weight of dry fat and the weight of the sample taken is water and dirt.

Palmnut and Coconut Oils.

The high **saponification** and **Reichert values**, and the low **iodine values**, of these two oils are characteristic, and afford ready means of distinguishing them from other oils and fats.

Coconut oil is said not to be adulterated. If required for lubrication, the most important test would be the estimation of **acidity**.

Tallow.

Tallow intended for lubrication, when melted in a test tube, should be clear, and free from more than traces of suspended matter. **Water,** if present, can be estimated as directed on p. 294. **Suspended impurities** (membrane, etc.) can be determined by dissolving a fair sample (10 to 20 grms.) of the tallow in chloroform or petroleum spirit, filtering through a weighed filter paper, washing out all fat with the hot solvent, and re-weighing the paper and contents. The latter, if sufficient in amount, may then be examined for possible adulterants, such as **starch, lime-soap,** etc. In genuine tallow, the percentage of insoluble matter rarely exceeds 0·2, and of water 1 to 1·5. (*Allen.*)

The **acidity** should, of course, be as low as possible, and should not in any case exceed 4 per cent. of oleic acid. This would exclude such adulterants as distilled grease stearin and rosin.

The **saponification value** may range from 19·0 to 19·8 per cent., and averages about 19·44. Paraffin wax (saponification value, nil) would lower the value; palmnut and coconut oils (sap. value 24·6 to 26·8) would raise it; bone-fat, cottonseed stearin, and cottonseed oil are without effect upon this constant.

The **iodine value** of genuine tallow has been found to range from 34·8 (*Thörner*, 32·7) to 46·2, according to published figures. Archbutt has met with apparently genuine tallow absorbing as much as 46·8 per cent. of iodine; possibly, but improbably, bone-fat or horse-fat might have been present, but not cottonseed stearin or oil. The average iodine value is about 40, according to Alder Wright, 43 according to Archbutt; Rowland Williams puts it at 40 to 41, Lewkowitsch at 36 to 40. The range is about the same both for beef and mutton tallow, but the average is probably lower for the latter. Any tallow having an iodine value above 47·0 would be suspicious, and might contain cottonseed stearin (88·5 to 104), cottonseed oil (101 to 117), horse fat (71·5 to 86), or bone fat (46·5 to 56). On the other hand an abnormally low value, say below 38, might be due to the presence of paraffin wax (4·0), palmnut oil (10 to 17·5), or coconut oil (8 to 9·5). It is obvious that a mixture of the above fats in suitable proportions might be made which would have the same iodine value as genuine tallow.

Cottonseed stearin and cottonseed oil, which are the most frequent adulterants of tallow, can, if present, be detected by the Halphen and Milliau **colour reactions** (unless they have been previously treated so as not to give these reactions). Pure fresh tallow gives entirely negative results. (See, however, Ryan's observation with lard, p. 279.) The nitric acid colour test (p. 277) would still be available, but the result must be interpreted [illegible] Allen states that tallow which has not been washed and [illegible] therefore, contains particles of blood, acquires a light-[illegible] when agitated in a melted state with nitric acid of 1·38 sp. gr. [illegible] cottonseed *oil or stearin*, L. Mayer recommends an examination of the 'oleine' obtained by allowing the melted tallow to crystallize for 18 hours at 35° C. and then squeezing the liquid portion through filter cloth. The iodine value of this should not exceed 55 if the tallow be genuine, but in presence of cottonseed oil or cottonseed stearin a much higher result will be obtained. The solidifying-point (titre test) of the fatty acids should also be determined; in the presence of the above-named adulterants it will be lower than 39° C.

Bone-fat leaves a variable but considerable proportion of ash on ignition. In 5 samples examined by Valenta the amount of ash ranged from 0·11 to 2·01 per cent.; average 1·32. This ash contains much calcium carbonate and oxide. As pure tallow and most, if not all, other vegetable and animal fats leave a scarcely weighable trace of ash, the detection of bone-fat should not be difficult. Commercial bone fat, according to Valenta's analyses, always contains a large percentage of free fatty acids (14·8 to 26·5); adulteration with any quantity of such bone-fat would be excluded by the 4 per cent. limit for acidity. Neutral bone-fat has the characters of a good lubricant. Bone oil (bone-fat oleine) is said to be used for lubricating clocks and watches.

Horse fat would probably communicate a yellow colour to tallow, would tend to make it soft, and would lower the melting-point of the fatty acids. This fat (as well as the above-mentioned) would lower the specific gravity of tallow at 60° F., which, however, is very rarely determined.

Paraffin wax, which is sometimes added to soft tallow, and usually reveals its presence by reducing the saponification value, can be estimated by determining the unsaponifiable matter, which, in genuine tallow, does not exceed 0·4 to 0·6 per cent. The same process would enable *rosin oil*, if present, to be detected, and also *wool fat*.

Palmnut and coconut oils, besides raising the saponification value (which no other likely adulterant would do), would increase the Reichert value and reduce the Hehner value. The commercial oils, which are usually very acid, would be excluded by the acidity test.

Valuation of Tallow.—By the soap and candle maker tallow is valued by the results of Dalican's titre-test (see p. 196). The 'titre' of tallow intended for candle-making (*i.e.*, the solidifying-point of the mixed fatty acids) should not be below 44° C.; tallow of lower titre is used for soap-making (*Lewkowitsch*). It does not follow that tallow for lubrication should be valued in the same way.

Tallow Oil.

Few analytical data have been published for this oil. Allen gives the specific gravity at 60° F. as 0·916, and the solidifying-point as 0° to +6° C. (32° to 43° F.). The oil should contain very little free fatty acid and, if genuine, should have an iodine value of, probably, 55 to 60.

'*Ox oil*' should be tallow oil expressed from beef tallow. '*Animal oil*' might contain the fat of other animals. Two samples of animal oil examined by Archbutt had a sp. gr. of 0·9187, iodine values of 59·7 and 60·4, and saponification values of 19·35 and 19·96 per cent. On cooling to 50° F., no crystals formed in three hours; but on lowering the temperature to 46° F., crystallization commenced, and slowly continued until the oil ceased to flow on inclining the tube. The low percentage of acidity (0·25 per cent.) and the high viscosity (nearly equal to that of rape oil) of the samples were noteworthy features.

Lard Oil.

The **specific gravity** of genuine American lard oil at 60° F. ranges from 0·913 to 0·919, according to Schweitzer and Lungwitz.* Ten samples examined by Archbutt ranged from 0·9162 to 0·9181; of these, two described as American lard oil had the highest sp. gr. (0·9180 and 0·9181), the remainder (probably of home manufacture) did not exceed 0·9170. Allen states that the sp. gr. should not exceed 0·9160. Adulterants such as cottonseed and maize oils would raise the specific gravity.

The **Maumené thermal value** (determined as described on p. 251) of the ten samples tested by Archbutt ranged from 41° to 46°, practically the same as in the case of olive oil. This is, therefore, a very valuable test, since most oils likely to be added as adulterants, except mineral oil, would increase the temperature reaction.

The **iodine value** of genuine lard oil varies considerably, owing to the variable proportion of olein. The interpretation to be placed upon the result of this test must therefore depend upon the congealing point of the oil. Schweitzer and Lungwitz, who have investigated this relation, determine the congealing-point as follows:—The oil is poured into a wide-mouthed bottle, immersed in a freezing-mixture of ice and salt, and stirred vigorously with a thermometer; the temperature is noted at which the oil shews the first sign of becoming cloudy. Any lard oil with higher iodine value than 70 should not shew signs of cloudiness above 40° F. The lard oils having iodine values of from 6[illegible] to 74 are generally pasty at 40° F.

The **saponification value** of genuine lard oil is about 19·42 to 19·53. Adulteration with rosin oil, mineral oil, or rape oil would lower the value.

Rosin oil or mineral oil, if present, would be detected and estimated by determining the **unsaponifiable matter**, which in genuine lard oil is less than 1 per cent.

Cottonseed oil would be detected by Halphen's or Milliau's **colour tests**; sesame oil by the furfurol test.

Genuine lard oil contains no arachidic or lignoceric acids; therefore, if these acids be found by **Renard's process** (p. 273), either earthnut oil or rape oil must be present.

Neatsfoot Oil.

Commercial neatsfoot oil may include the oil from the feet of sheep, pigs, horses and other animals, and is liable to extensive adulteration with vegetable oils, fish oils, mineral oils, and, doubtless, rosin oil. When properly prepared from fresh feet, this oil contains less than 0·5 per cent. of **free fatty acid**; but the commercial oil, owing either to adulteration or to carelessness in manufacture, sometimes contains a very large percentage of acidity. According to Mr. E. Grant Hooper,* as much as 34 per cent. of free oleic acid has been found.

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* *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 129.

There is not sufficient data for defining the natural limits of variation of this oil; the numbers in the table on p. 303, based upon results obtained chiefly by Lewkowitsch, and by Coste and Parry, must be regarded as approximate.

Seed oils, such as cottonseed and maize, also fish oils, would raise the **specific gravity**, **iodine value**, and **Maumené value**. Cottonseed oil would be detected by Halphen's and Milliau's **colour tests**; sesamé oil by the furfurol test.

Mineral and rosin oil would be found in the **unsaponifiable matter**, which, in genuine neatsfoot oil, probably does not exceed 1 per cent.

Whale Oil.

Owing to the low price of whale oil, the only adulterants likely to be added to it are rosin oil, mineral oil, cheap fish oils, and possibly cottonseed or maize oil. The examination of a sample intended for lubrication should be first directed to the determination of **acidity**; 21 samples of 'white' whale oil, tested by Veitch Wilson, contained from 1·0 to 5·5 per cent. of free fatty acid, the average percentage being 2·14. The search for adulterants may then be made, together with a careful comparison of the oxidizing property of the oil as compared with a standard sample of good quality.

Schweitzer and Lungwitz,† who have examined a large number of pure whale oils refined and sold in the United States, state that refined whale oil (*i.e.*, whale oil freed from 'stearin' by cooling and straining) should be clear and of a pale yellow colour.

The **specific gravity** should lie between 0·921 and 0·923 at 60° F., the **saponification value** between 19·0 and 20·0 per cent., and the **iodine value** between 120 and 130. The mixed **fatty acids should melt** completely at or below 20° C.; a higher melting-point would indicate the presence of cottonseed, maize, or fish oil. Small percentages of these oils are said to cause the appearance of crystals in the fatty acids at the ordinary temperature, whilst the fatty acids from pure whale oil shew no signs of crystallization. Cottonseed oil would be detected by the **Milliau test**; mineral or rosin oil would be found in the **unsaponifiable matter**, and could readily be identified by the tests given in Chapter VII. Section B (p. 209).

Sperm Oil.

No means of distinguishing southern and Arctic sperm oils except by the smell and appearance, much less of detecting one when mixed

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* *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 5.

† *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 130.

[illegible] The most important difference [illegible] melting-[illegible] a sufficient number of authentic [illegible] what this [illegible] refractometer [illegible] sperm oil being [illegible]

[illegible]

[illegible]	1. [illegible]	2. [illegible]
[illegible]	[illegible]	Golden yellow; paler than No. 1.
[illegible]	[illegible]	Fishy; more pungent than No. 1.
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	− 13
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	nearly white [illegible]	nearly white [illegible]

[illegible] Samples of the two oils kindly examined for us by Mr. W. [illegible] refractometer gave an identical reading of [illegible] For the samples referred to we are indebted to Mr. J. F. [illegible] may be of interest to give here the complete [illegible] of the examination of these samples. (See Table XCII.)

The problem, therefore, of detecting bottlenose oil in sperm oil being, for the present at any rate, insoluble by chemical methods, the two oils will be considered as identical in the following remarks.

The **specific gravity** of genuine sperm oil ranges from 0·878 to 0·884, and would be raised by the addition of any fixed oil or fat; this could be corrected by the addition of light mineral oil, but not without lowering the **flashing-point**, which, according to Allen, is as high as 480° F. in the case of genuine sperm oil. Out of 93 samples of sperm oil tested by Veitch Wilson the flashing-points (closed test) of only 3 samples were below 410° F., viz.:—one sample 400° and two 390°. The others ranged from 410° to 485° F., and the averages were 457·5° F. for southern sperm and 446·2° F. for Arctic sperm. There are pure mineral lubricating oils having the same specific gravity and viscosity as sperm oil, but their flashing-points are lower than 400° F.

The low **saponification value** of sperm oil is characteristic, but is not to be relied on as a test of purity, since a mixture of a cheaper fixed oil with mineral oil could be made to have the same value. Lobey de Bruyn has found, however, that in sperm oil adulterated with such a mixture the presence of mineral oil can be detected by *Holde's test* (p. 210), since the higher alcohols formed by saponifying sperm oil do not separate at once on adding water, but remain for a considerable time dissolved in the soap solution.

The most reliable means of detecting the adulteration of sperm oil is to isolate and examine the **unsaponifiable matter.** Genuine sperm oil yields from 36·3 to 41·5 per cent. of unsaponifiable matter, consisting entirely of wax alcohols easily soluble in cold rectified alcohol; if the unsaponifiable matter obtained from 5 grms. of a sample of sperm oil be normal in amount and completely soluble in 2 c.c. of cold alcohol of sp. gr. 0·834, the sample is most probably genuine. For further information as to the properties of the wax alcohols from sperm oil, see Table LXI. (p. 224); also page 221. For the analysis of mixtures containing sperm oil and mineral oil, see p. 233.

Porpoise and Dolphin Jaw Oils.

Their remarkably high **Reichert value** is sufficient of itself to identify these oils. The high **saponification value** and low **iodine value** are also characteristic. The results obtained by the examination of a sample of Kelley's watch oil are given on p. 116.

D.—BLOWN OR THICKENED OILS.

Blown rape oil and blown cottonseed oil ('lardine') are usually pale-coloured and extremely viscous oils having a nauseous odour. The only natural oil which they at all resemble is castor, and from it they are easily distinguished by their sparing solubility in alcohol.

1-2 c.c. of castor oil, if shaken in a test tube with 10 c.c. of 90 per cent. alcohol, will dissolve easily, but the same quantity of blown oil remains apparently insoluble.

For the detection of blown oils in castor oil, see *Castor Oil* (p. 308). For their identification when mixed with mineral oil, the following characteristics are available, viz.:—the dark colour produced on saponifying them with alcoholic potash solution; the high specific gravity at $\frac{100^\circ}{100^\circ}$ C. of their insoluble fatty acids (p. 177); the considerable proportion of soluble non-volatile acids formed by their saponification (p. 118); the comparatively low iodine value and high acetyl value of the insoluble fatty acids (see pp. 246 and 240). The soluble non-volatile acids were estimated by Thomson and Ballantyne by collecting the filtrate and washings from the insoluble acids, distilling to dryness and extracting the dry residue with ether. After expelling the ether by evaporation, the acids were weighed and then titrated with standard alcoholic potash solution. For the Reichert-Meissl value of blown oil, see p. 232.

Blown oils have not been sufficiently investigated to enable data to be given for distinguishing them with certainty from one another. Blown cottonseed oil may be recognized by the high melting-point of the fatty acids (41° C.), and may also be distinguished from blown rape oil by its higher saponification value, provided the oils compared have [illegible] the same or nearly the same degree of oxidation, *i.e.*, [illegible] specific gravity about the same number of units [illegible] gravities of the natural oils. Thomson and [illegible] by experiments with such widely different oils [illegible] that the specific gravity and iodine value similarly [illegible] in almost exactly the same ratio during oxidation [illegible] in the specific gravity of 1 unit in the third decimal [illegible] by an average fall of 0·757 per cent. in the [illegible] oil and 0·75[illegible] per cent. in that of sperm oil. [illegible] value of the rape oil was, however, more rapid [illegible] of the blowing process, averaging 0·963 per unit [illegible] the first 5 hours. Similarly, the increase in the [illegible] was more rapid at first, for, by the time the rape [illegible] from [illegible] to [illegible], the saponification value [illegible] per unit; but, after the oil [illegible] had increased in sp. gr. to [illegible], the saponification [illegible] only risen to 184[illegible], or an average, during the whole [illegible]

[illegible] should be examined for acidity in the same manner as [illegible] made from. As stated on p. 117, the tendency of [illegible] process is to increase the percentage of free acid.

E.—MIXED LUBRICANTS.

Mixed lubricants may be either oils or greases, and may or may not contain soap. For the detection of soap, see section W, p. 291.

I. **Mixed oils and greases free from soap** may contain mineral oil, rosin oil, or coal-tar oil, together with a fixed oil, fat, or wax; the fixed oil may be a blown oil. An approximate analysis may frequently be made by Gripper's method (Section D, p. 214).

A more exact analysis may be made by isolating and weighing the unsaponifiable matter (section E, p. 215), and then determining its properties and nature (section F, p. 219). By recovering the mixed fatty acids from the soap solution, and submitting them to examination (section G, p. 224), the fatty ingredient of the mixture may frequently be identified. Obviously, the problem becomes simplified when the mixed oil is purchased to a specification stating what the nature and proportion of the component oils must be. For the analysis of mixtures containing sperm oil or wool fat and mineral oil, see p. 233.

II. **The analysis of oils and greases containing soap** is conducted in the following manner:—

10 grms. of the sample are stirred with ether in a small beaker until dissolved or thoroughly disintegrated. The liquid is then rinsed with ether into a separating funnel and shaken several times, with 10 c.c. each time of hydrochloric acid (sp. gr. 1·10) to decompose all soaps and extract the bases. The ethereal liquid is then washed with water until free from acid.

Acid extract.—This contains the metals existing as soap. It is first washed with a little ether to remove mechanically mixed oil, the ether being added to the main ethereal solution. The liquid is then placed in a beaker, covered with a clock-glass, and heated on a warm water bath until the dissolved ether has boiled away. It is then poured into a basin, evaporated to dryness on a steam-bath, redissolved in hydrochloric acid and water, filtered, and the metal or metals which were qualitatively detected in the ash may be estimated in the clear solution.

Ethereal solution.—This contains the neutral oil (fatty and mineral), together with all fatty and resin acids which existed in combination with the metal as soap. In order to extract the fatty and resin acids, the solution is shaken with 50 c.c. of a 2 per cent. solution of caustic soda (10 per cent. caustic soda solution, 20 c.c.; rectified spirit, 10 c.c.; water, to 100 c.c.). The shaking should be continued for ½ to 1 minute and be not too vigorous, lest an emulsion be formed. After separation has taken place, the soda solution is drawn off into another separator, and the ethereal solution is further shaken with 10 c.c. quantities of the dilute soda solution until all fatty acids are extracted; it is then washed several times with water. The mixed alkaline extract is first shaken with a little ether, which is added to the neutral ethereal solution, it is then acidified, and the liberated fatty (and resin) acids are extracted with ether and weighed. The neutral ethereal solution is also evaporated and the residue weighed. We thus obtain:—

(*a*) *Metallic oxides, existing as soap.*

(*b*) *Fatty (and resin) acids existing in the free state and as soap.*—Estimate the *free fatty acid* in a portion of the original sample as directed in section A, p. 201; if worth while, deduct this amount from the total, and multiply the remainder by 0·97 to reduce to anhydrides; add the metallic oxides; the sum is the amount of dry *soap*. *Resin*, if detected by Liebermann's test, may be estimated by Twitchell's method. *Phenols*, from coal-tar oil, if present (very rarely), would have to be separated from the fatty and resin acids by distillation with steam.

(*c*) *Residual (neutral) oil.*—This may contain any or all of the following:—*mineral oil*, *rosin oil*, (*coal tar oil*), *fixed oil*, *wax*, and, possibly, *free wax alcohols*. It must be analysed as directed above, p. 317, E, I.

In addition, the grease may contain:—

(*d*) *Water.*—This is determined as directed in section Z, p. 293.

(*e*) *Non-fatty ingredients*: such as *plumbago*, *talc*, *sulphur*, etc.—These will for the most part remain insoluble and be drawn off with the aqueous extract. They must be filtered off and examined separately.

(*f*) *Excess of base.*—This is detected and estimated by determining the combining weight of the fatty acids and ascertaining whether the amount of base found is more than sufficient to saturate them.

CHAPTER IX.

THE MECHANICAL TESTING OF LUBRICANTS.

Introductory.—Although the ultimate decision of the engineer concerning the lubricating value of any oil, grease, or fat must necessarily be governed by the results obtained in everyday work, yet when lubricants have to be purchased in large quantities it is advisable to have some means of testing them mechanically. Until comparatively recent years, mechanical methods were chiefly relied upon in the testing of lubricants. Owing, however, to the introduction of new lubricants of mineral origin, and the increasing extent to which adulteration has been indulged in, the necessity of making careful chemical analyses of oils, etc., and the determination of their more important physical properties in the laboratory, have become more and more recognized.

Improved chemical and physical methods of analysis have rendered it possible to determine accurately, and often state in absolute measure, the value of many properties of lubricants which mechanical testing machines can only give very imperfectly. Mechanical methods have, therefore, largely yielded to chemical ones, and the value of the oil-testing machine has been somewhat lost sight of. It must not be forgotten, however, that it is only by special frictional methods involving the disappearance of the oil pressure-film (see p. 64) that the 'oiliness' or 'greasiness' of lubricants can be measured. When the conditions of speed, etc., are such that the pressure film can form, the frictional results simply arise from the viscosity of the lubricant and the curvature of the rubbing surfaces. The chances of being misled by attaching undue importance to viscosity were but small and unimportant when vegetable and animal oils only were used. The chemist or engineer had then merely to ascertain whether the sample was genuine rape, sperm or other oil, as the case might be, the relative lubricating powers of the pure oils under different conditions being fairly well known. Of late years, however, numerous new viscous liquids of mineral origin (hydrocarbon oils) of varying lubri-

[illegible] have been introduced, and to ascertain their lubricating [illegible] mechanical tests made with specially [illegible] to be resorted to.

[illegible] to be readily made, machines have been [illegible] so arranged that any load [illegible] may be [illegible] method of applying the [illegible] accurately measured.

[illegible] of **Mechanical Testing.**—The [illegible] tests of lubricants may [illegible] in view, one being to measure the [illegible] determine the relative [illegible]

[illegible] under which the oil is to work [illegible] the results [illegible] variation in the method of [illegible] in the rubbing surfaces, has an [illegible] frictional resistance. If, [illegible] on the other [illegible] greasiness of a lubricant, it is necessary [illegible] results due to viscosity. Imper[illegible] of this being done most satisfactorily [illegible] that whereas at low speeds greasiness is an [illegible] perfect lubrication at high speeds viscosity plays [illegible]

[illegible] are also the most suitable conditions [illegible] resulting from [illegible] at high speeds is a [illegible] by the formation of the [illegible]

[illegible] of oils may also be [illegible] by observing the changes which [illegible] has remained exposed for some hours.

[illegible] machine is thus, from a practical point of [illegible] contrivance, and should be regarded [illegible] part of the equipment of a modern oil-testing [illegible]

[illegible] machines have furnished data which have en[illegible] mathematical theory of [illegible] tests, with the result that the part [illegible] of the frictional resistance between [illegible] bearings is clearly understood. Indeed, [illegible] that mechanical testing machines have yielded [illegible] information which is slowly but surely leading [illegible] for old methods of lubrication new ones which [illegible] efficiency.

Design of Oil-testing Machines.—Various forms of machine [illegible] been built and used for testing purposes, varying in design according to the information they are desired to convey, and which can be summarized as follows:—

(1) Comparative oiliness or greasiness.
(2) Frictional effects due to viscosity.
(3) Effects resulting from different methods of applying the lubricant.
(4) Effects produced by different metals working in contact.
(5) Effects of temperature on friction.
(6) Effects produced by different loads.
(7) Effects produced by varying speeds.

A description of a few only of the different types of machine designed for ordinary testing work, and which have been used for experimental purposes, will here be attempted; the nature of the tests which may be made with them being in some cases given. This can, however, only be done in an incomplete manner; for the subject is an extremely complex one, each kind of machine requiring different treatment, and being capable of affording valuable information if placed in the hands of an operator who has a knowledge of the theory of lubrication and has had some experience in the management of machinery.

It must be remembered that every change of speed, load, method of lubrication, temperature, form of bearing, and condition of rubbing surface has some, often considerable, effect upon the frictional resistance obtained with each lubricant, and, therefore, that the problems arising in the course of such experimental work are often very intricate and difficult of solution. If, for instance, a number of oils tested under small loads fall in a particular order of merit as regards friction-reducing power, on testing them with heavier loads the order will be found to have somewhat altered. Changes of speed produce even more marked differences, sometimes increasing and sometimes decreasing the friction. These points have been dealt with in some detail in Chapter IV., on 'The Theory of Lubrication.' Much, however, still remains to be learned concerning the frictional resistances of bearings when running at low speeds with different loads. This point will be briefly discussed in Chapter X., on 'The Design of Bearings.'

Mechanical testing machines vary greatly, not only in the shape of the contact surfaces, but also as regards the indications which they give concerning the degree of frictional resistance encountered. In some machines the rotating surface assumes the form of a wheel or drum upon which a bearing block is pressed. In others it is a disc, the flat side of which is pressed against a similar disc. But in the machines most commonly used the contact surface takes the form of a cylindrical journal a few inches in diameter, upon which rests a weighted bearing-block or brass.

It has been shewn (p. 64) that the conditions under which lubrication can be effected with cylindrical rotating surfaces are quite different from those which obtain with discs or other plain surfaces. It will therefore be convenient to deal first with the rotating cylindrical or drum form of machine, and subsequently with machines that give the frictional resistances, etc., between discs and plain surfaces.

Cylindrical or Drum Machines.—*Thurston's Oil-Testing Machines.*—These machines, which are made by Messrs. W. H. Bailey & Co., Albion Works, Salford, Manchester, are frequently used in England and America. They are convenient, and are easily kept in order; for scientific work, however, they are hardly suitable. Two sizes are made, one, a small machine, occupying but little space and requiring very little power to drive it, and another, of much larger form, suitable for railway work.

Of these the larger machine only will be described. It has a cylindrical journal against which work two brasses, one above and the other below. Slung from the upper brass is a hollow pendulum containing a strong spring, the upper end of which lifts the bottom brass against the journal, whilst the lower end depresses the pendulum and helps to weight the upper brass.

Fig. 73 is a side elevation, with the brasses and pendulum in section, and fig. 74 an end elevation of this machine. The hollow shaft A, driven by a cone pulley B, is mounted on a strong cast-iron stand, the forked ends of which form the bearings upon which it runs. One end of the shaft projects beyond the bearing and is fitted with a bush C, on the outside surface of which the oil tests are made. This enables various metals to be used as bearing surfaces, for the bush can easily and quickly be removed and another put in its place. The box E E, forming the head of the pendulum, holds the two bearing brasses D, on which the pendulum is slung from the journal. In order to enable the operator to vary the pressure of the brasses against the journal at will, the pendulum is constructed as follows. A wrought-iron tube H, shewn in fig. 73, is screwed into the axle-box E, which passes round the journal and holds the bearings D in position. In the upper part of this tube is loosely fitted a distance piece O, which, by the action of a strong spring below it, forces the under brass against the journal. The end of the spring does not press directly against the distance piece, but upon a screwed washer, K, threaded upon a rod M, which has a square end, by means of which it can be rotated. At its lower end the spring rests upon a cap I, screwed to the tube H, and by it the stress on the spring is brought to bear upon the upper bearing D, as well as on the lower one. To compress the spring and increase the load on the bearings, the square end of the rod M is rotated, which actuates the washer K, to which is fixed the index finger. A scale, screwed to the tube H, shews the weight per square inch and the total weight on the brasses for every position of K. A ready means of taking the pressure off the brasses is furnished by the nut P, which can be screwed down until the key R, against which it presses, separates the distance piece O from the bearing.

It is evident, that any friction between the blocks D and the journal C will cause the pendulum to move in the direction of revolution of the shaft, and the greater the friction the further will the pendulum swing. As the moment of resistance of the pendulum varies with its weight and the position of its centre of gravity, it is possible to vary very considerably the scale on the arc W. When

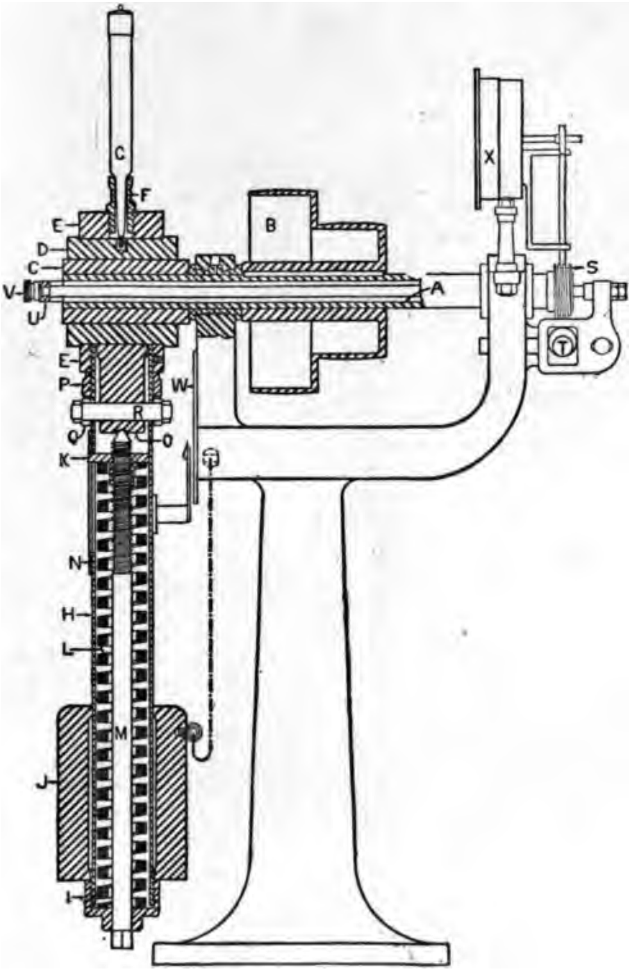

Fig. 73.

an open scale is required, the weight J is removed; a counterbalance can also be placed on a pillar screwed into the top of the axle-box E. Of course, each alteration of the position of the centre of gravity of

[illegible]

Several methods of calculating the area of contact of a brass have been adopted. The plan commonly followed has been to multiply the length of the brass (l) by the diameter of the journal (2r); 2rl is then the projected area of the bearing on a diametral plane, or, as it is commonly called, the nominal area. But it is impossible, except with light loads, to make a bearing run satisfactorily when the brass embraces as much as one-half of the journal. In practice, the sides have to be cut away until the actual arc of contact is only one-fourth or one-fifth of the circumference; and as at all ordinary speeds, with good lubrication, the friction is nearly proportional to the actual contact area, it is better to substitute actual for nominal areas by multiplying the length of the arc of contact *a* by that of the brass *b*.

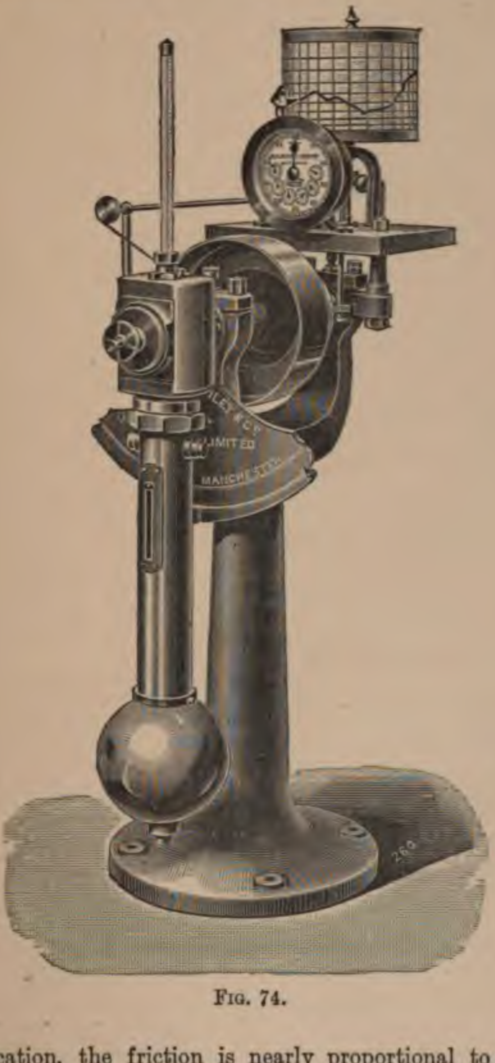

FIG. 74.

Thurston graduates the scales on his machine on a nominal area basis; however, from the following formulæ the scales can be graduated to agree with actual areas of contact, and from them the true coefficient of friction, etc., can be obtained.

Let r = radius from centre of journal to centre of gravity of pendulum.
r_0 = radius of journal.
W = weight of pendulum.
a = width of brass (*i.e.*, length of arc of contact).
b = length of brass.
P = total pressure of brasses on journal.
p = pressure per sq. in.
T = load on spring.
θ = angle between pendulum and perpendicular through axis.
μ = coefficient of friction.
F = total frictional resistance.

When θ is equal to 90°, $Wr = Fr_0$ . . . . (1)

When it is equal to any other angle, $Wr \sin\theta = Fr_0$ . . . (2)

$$\text{Therefore } \sin\theta = \frac{Fr_0}{Wr} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From equation (3), the graduations on the arc W are marked off so as to give the total frictional resistance F for any angle.

From equation (2), the total friction $= \dfrac{Wr \sin\theta}{r_0}$. (5)

When the pendulum is a heavy one, and the compression on the spring is such that the load on the brass is small, the load on the upper brass is, at all small inclinations, $P_1 = T + W$ . . . . (6)
and on the lower brass, $P_2 = T$ . . . . (7)

When T is large and W is small, it is sufficiently accurate to make

$$P = 2T + W \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and from this the left hand side of the scale N is graduated.

Under similar circumstances, the pressure per sq. in. is $p = \dfrac{P}{2ab} = \dfrac{2T+W}{2ab}$ (9)

From this equation, the graduations on the right hand side of the index plate are deduced.

The readings given by the index plate N and the arc W enable the coefficient of friction to be calculated directly, for

$$\mu = \frac{F}{P} = \frac{\text{Reading given by arc W}}{\text{Reading given by index N}} \quad . \quad . \quad . \quad (10)$$

When experimenting with small loads on this machine, it must be borne in mind that the load on the upper brass is always greater than on the lower one. Under such circumstances, the maximum load is given by equation (6)

and the pressure per sq. in. is $p = \dfrac{P_1}{ab} = \dfrac{T+W}{ab}$ . . . . . . (11)

It is impossible to always accurately measure the friction due to the upper and lower brasses respectively. When the lubrication is good, and the speed of rubbing over 3 feet per min., the friction proportional to the area of the brass in contact with the journal d independent of the load, but, when the speed is small, this is t the case, and it is impossible to obtain *accurately* the coefficient friction of either the upper or lower brass.

Methods of Working Thurston's Machine.—When about to use the achine, the pendulum should be removed from the journal C, and e pointer adjusted by turning the screw M, projecting from the lower d of the pendulum, until the index K shews the pressure it is desired put upon the brasses. To enable the brasses to slide easily over the urnal, they can be forced apart by screwing down the nut P, which ill be found immediately under the axle-box E. When this has en done, the brasses will slide freely off the journal.

Before testing each sample of oil, the pendulum must be removed d the brasses and journal cleaned with great care; for the effect an oil may be felt in successive tests long after a new lubricant s been applied. This results from the contamination film, which mains even after the surface has been rubbed bright and apparently ean. Alcohol, gasoline or benzine, which themselves evaporate very mpletely and leave the surfaces they have wetted dry, serve to move the lubricant from the pores and crevices of the surfaces and so from the oil-ways, etc. One or other of these liquids should be ely used after each test, care being taken to leave no worsted, tton, or other foreign material on the surfaces, and to allow ample ne for the spirit to evaporate before putting on the fresh lubricant.

Before releasing the nut P and allowing the load to come on the asses, it is advisable to moisten the journal with oil and to allow e machine to run with the weight of the pendulum alone on the ass, so as to distribute the lubricant. When this has been satis- ctorily accomplished, the machine should be stopped, and, by turning e nut P, the lower brass entirely released, so that the spring may ess it against the journal. The machine may then be again started, the cessary speed having been secured by adjusting the gearing, straps, motor resistances, a proper rate of feed being kept up during the periment. The bearing should not be allowed to run dry, for the mporary decrease of friction, which often occurs before the surfaces ize, may lead to erroneous deductions.

When not fitted with an automatic recording apparatus, observa- ns of the frictional resistance encountered, as well as of the mperature of the air and journal, should be made at intervals of e or more minutes, until the readings become constant, when the periment may be terminated.

The ordinates on the recording drum shew the total frictional sistances, and the abscissæ the number of revolutions made by e journal. On one such diagram, during the first five hundred volutions, the test shewed that the friction first increased and then ll rapidly until the temperature of the bearing reached 100°, while, ter 20,000 revolutions, both friction and temperature remained nstant.

[illegible] marked effect produced upon the frictional resistance
[illegible] a small change in the shape or condition of the
[illegible] pad or bath lubrication is resorted
[illegible] tested in the machine must be compared with a
[illegible] standard lubricant, such as genuine
[illegible] This is a good lubricant, and if preserved in the dark
[illegible] keeps well. To ensure a correct com-
[illegible] make several tests in succession, both
[illegible] of the sample under examination—an average
[illegible]

[illegible] resistances, and to obtain results almost
[illegible] the viscous properties of the lubricant, the
[illegible] one-fourth of the circumference of the
[illegible] their surfaces, but the lubricant
[illegible] means of pads placed at the sides of the
[illegible] to have a little side play in
[illegible] place themselves in that position
[illegible] whilst the oily pads ensure
[illegible] The speed of rubbing
[illegible] feet per min. When these conditions
[illegible] it has been demonstrated that
[illegible] the viscosity of the oil, and
[illegible] nature of the contact surfaces or the
[illegible] fairly viscous oils, light
[illegible] pressure-film forms properly
[illegible] It will, of course, be under-
[illegible] and that the viscosity
[illegible] with the frictional
[illegible] when trials are
[illegible] results entirely from the
[illegible] ordinary temperatures is most
[illegible] friction for the lubricating
[illegible] temperature of the surrounding
[illegible] reduced. Mineral
[illegible] of the same
[illegible] friction, for the former
[illegible] somewhat more rapidly than
[illegible] this kind by no means shew
[illegible] for the actual
[illegible] produced by increased temperature
[illegible] with the viscometer.

[illegible] obtained by mechanical oil-testing
[illegible] been pointed out, the determination of
[illegible] greasiness of liquids and soft solids; pro-
[illegible] lubricants to prevent the abrasion and
[illegible] The method which has been
[illegible] such properties has been to imper-
[illegible] and thus allow the surfaces to approach

each other so closely that the oil pressure-film cannot form properly. It is essential that the bearing surfaces should come into close juxtaposition if we are to obtain a correct estimate of the value of different brasses, bronzes, and white metals, for these metals are only used to enable the bearing to carry its load without suffering abrasion when the conditions of running are such that the oil pressure-film, maintained by the viscosity of the lubricant, cannot form, and the surfaces approach each other closely.

For tests of this kind, the brasses should be allowed to extend over only about one-fifth or sixth of the circumference of the journal, and the lubrication may be supplied by well-moistened pads at the sides. With a load of 150 or 200 lbs. per square inch, a series of tests made at speeds varying from 1 to 100 feet per minute will enable a very characteristic curve of the lubricant to be plotted. A series of tests made with loads increasing to 500 lbs. per square inch or more, the speed being, say, 1 foot per minute, will also give results which vary with different lubricants and bearing metals.

The loads must, of course, be varied so as to meet as nearly as possible the conditions under which the lubricant will work in practice.

For the purpose of distributing the lubricant evenly over the journal, and of preventing both it and the brasses from wearing in ridges, the latest form of Thurston's machine is fitted with an eccentric T, fig. 73, which slowly moves the brasses backwards and forwards along the journal. With this device attached, the readings obtained by making a series of tests of the same lubricant shew fewer and smaller discrepancies than can be obtained when the brass has no lateral play.

Thurston states that his machine may be used for the purpose of ascertaining the gumming properties of lubricants, and also their durability. No doubt with care some idea on these points may be obtained by the use of mechanical testers, but such tests are usually better made by physical and chemical methods.

Many lubricants when exposed to the air take up oxygen and become thick, *i.e.*, they gum. This change in the viscosity may be scarcely appreciable when the liquid is kept in bulk, but when it is spread over a bearing as a thin film and exposed to the air, it may rapidly become a sticky mass and cease to lubricate. Although the extent to which this change takes place can be more satisfactorily measured by methods which have already been fully described (p. 254 *et seq.*), useful information may sometimes be gained by measuring the effect produced upon the friction coefficient. The bearings should be lubricated with just sufficient oil to wet them well and yet not run off. The journal is then run at a speed of about 100 feet per minute with a very light load, and the friction and temperature noted when they have ceased to vary appreciably. Both brasses are then removed, and the contact surfaces, protected from dust and dirt, are allowed to remain exposed to the air for a day or two. The brasses are then replaced in the machine and a test made as before. If the oil has thickened, the friction and heating will be greater than before.

[illegible] which are liable to gum are also liable to become [illegible] bearing surfaces. Metallic soaps are thus formed, [illegible] cause it to thicken. Mineral [illegible] may contain light constituents [illegible] For these and [illegible] temperature of a bearing [illegible] not prove that the oil has really [illegible]

[illegible] may either be supplied con- [illegible] run off the bearing, [illegible] with a definite quantity of [illegible] against the sides of the journal. The [illegible] until the friction and temperature [illegible] after starting, the lubricant [illegible] temperature becomes steady, and the [illegible] however, as the lubricant [illegible] of the bearings, or with [illegible] the friction and temperature begin to [illegible] quantity of which will keep the [illegible] best to use for the par- [illegible]

[illegible] and are little affected by the [illegible] which they test, they continue to [illegible]

[illegible]

[illegible] —The [illegible]

[illegible] is then stopped [illegible] that the conditions [illegible] to merely [illegible] The machine is shown in [illegible]

[illegible] —The [illegible] is a modified form [illegible] different arrangement of [illegible] is fitted with a [illegible] to record the [illegible] meter to measure the [illegible]

[illegible] compared with its length, [illegible] nearly half the cir- [illegible] a system of levers and weights. It is [illegible] same way as the Ingham and Stapfer [illegible] similar information. Tests for oiliness and greasiness can only be properly made by cutting away the brasses, increasing the loads, and running at slow speeds.

Stroudley's Oil-Testing Machine.—This machine was built so as to make the conditions of running closely resemble those of a carriage or locomotive axle. It has only one bearing, which rests upon the revolving axle A, fig. 76. The bearing carries the beam C, which has knife edges at the ends upon which rest the suspending links and weights for applying the load. G is a small beam and pan.

When the journal is in motion the link D is depressed, but by placing weights in the pan of the small balancing lever it is raised until the pointer P indicates that the beam is in its normal position. The weights in the pan are then a measure of the frictional resistance. H is a small eccentric and wheel driven by a worm on the main shaft. It keeps the brass continually moving to and fro, side play being necessary to cause the surfaces to remain free from grooves. M is an oil-pad, which keeps the journal constantly lubricated, N is a siphon lubricator, R is a revolution counter, and T a thermometer to shew the temperature of the journal.

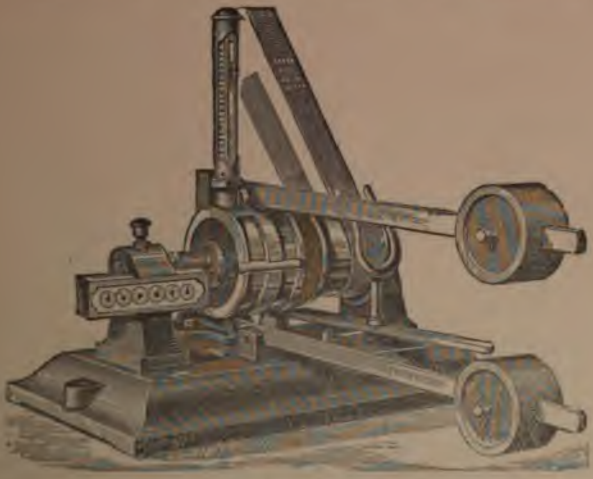

FIG. 75.

This machine, Prof. Goodman says, when accurately adjusted, runs rather more steadily than Tower's machine, consequently there is less liability to error in taking readings. The lubricating arrangements are easily accessible, and the bottom of the shaft is quite open. Then again the loads are very accessible, being quite free from the framing, a very important point, considering that the weights often amount to as much as 2 cwts. each. But the disadvantage in the machine is that the most scrupulous accuracy is required in making the weights exactly equal, while the weight, beam, and links must also be exactly balanced. The balancing of the weights and beam is effected as follows:—

After the beam has been machined very accurately, so that the jaws into which the brasses fit are central with the knife edges on which the weights hang, a temporary knife edge is fitted in the centre of the jaws, and the beam itself balanced upon it. The links to carry the weights having been hung on and balanced, the knife edge is removed, and the brass having been fitted in is placed on a short mandril which it exactly fits. The whole is now placed on a smooth level plane, and the beam again balanced by adjusting the brass in the jaws until the centre of the mandril is central with the knife edges; by this means a practically frictionless vibrating balance is obtained. The weights themselves are placed on the links, and each pair balanced and marked.

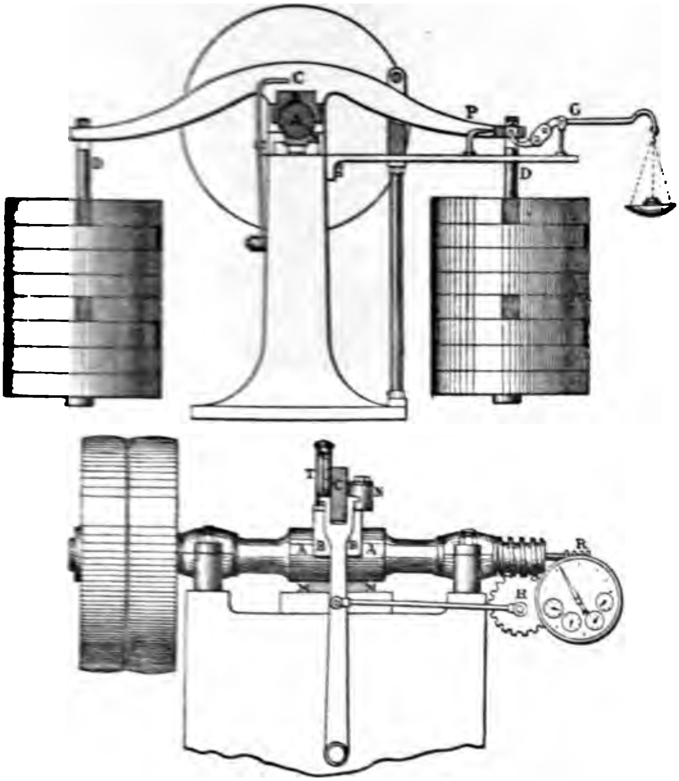

Fig. 76.

After the machine has been running for some time its balance is disturbed, unless the direction of motion has been periodically reversed. This results from the wear being chiefly confined to the 'off' side of the brass, a point to which attention has already been called. The inequality of wear is occasionally very rapid under heavy loads, a few days' hard running causing the brass to wear ·01 inch out of centre. Suppose the load to be 1 ton, or 2240 lbs., which, with an equivalent length of arm of 72 inches, gives an error of

$$\frac{0{\cdot}01 \times 224}{72} = {\cdot}311 \text{ lbs.} \quad . \quad . \quad . \quad (12)$$

in the scale pan; this, with a 7-in. shaft, becomes an error of ·0028 in the coefficient of friction, or an error in some instances of as much as 100 per cent. Thus, a very small error in construction, or any displacement due to uneven wear, has a serious effect upon the readings, a possibility which should never be lost sight of.

The coefficient of friction is calculated as follows:—

Let r_0 = radius of journal.
P = weight on brass.
F = total frictional resistance.
r = length of main beam.
$\frac{y}{x}$ = leverage of scale beam.
W = weight in scale pan.

Then

$$\frac{Wry}{x} = Fr_0 \quad (13) \therefore F = \frac{Wry}{xr_0} \quad . \quad . \quad . \quad . \quad (14)$$

and

$$\mu_1 = \frac{F}{P} = \frac{Wry}{Pxr_0} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Beauchamp Tower's Experimental Testing Machine.—With this machine, a series of experiments was made on the friction of journals by a Committee of the Institution of Mechanical Engineers.* By using pad and bath lubrication, and running the journals at moderately-quick speeds, results were obtained which were closely in agreement with each other, and which demonstrated that under some conditions of running the friction of a journal is extremely small, and is independent of the nature of the contact surfaces. A theoretical examination by Prof. Osborne Reynolds † of the results obtained shewed that the friction was wholly due to the viscous properties of the lubricant, and independent of the nature of the surfaces or of the oiliness or greasiness of the lubricant.

As the viscosity of a lubricant can be more satisfactorily determined by the use of a properly-constructed viscometer, and the conditions obtaining at high speeds do not give any information concerning the oiliness of the liquid used, nothing in the nature of a test of the quality of oiliness can be made with Tower's machine, unless the conditions of speed and load be such that the oil pressure-film does not form. However, as the results obtained with this machine enabled the true theory of 'perfect' lubrication to be worked out, a description of it will not be out of place.

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* *Pro. Inst. Mech. Eng.*, 1883, p. 632.

† *Phil. Trans. Roy. Soc.*, 1886, p. 165.

Upon the rotating journal A, fig. 77, rests a brass bearing B, held in a frame C. A knife-edge, secured to this frame exactly beneath its centre, supports the weights by means of which the load is applied. The turning moment, resulting from the friction of the journal and brass, is balanced by means of weights placed in the scale pan slung from the light iron frame D. A pointer E and graduated scale indicate when the frame is in its normal position. The bottom of the journal is kept well lubricated by the oil-bath H into which it dips.

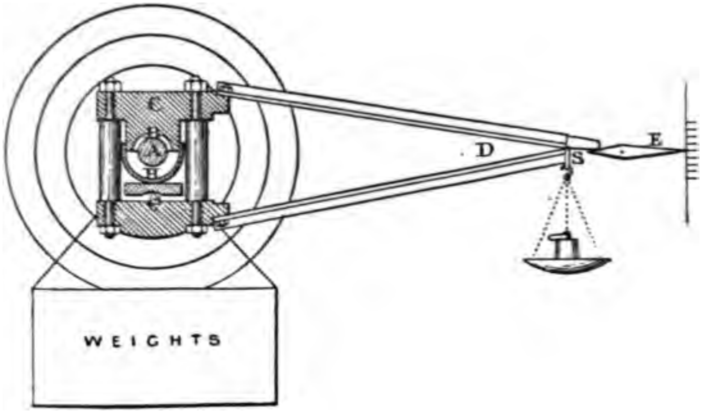

FIG. 77.

When working with a weight w in the scale pan, the coefficient of friction is obtained as follows:—

$$Fr_0 = wr \therefore F = \frac{wr}{r_0} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and

$$\mu_1 = \frac{F}{P} = \frac{wr}{Pr_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

When working with a pointer E and no scale pan, and measuring the angle θ, the centre of gravity of the weight being displaced a distance r^1 on either side of the centre of the journal, $W = P$,

$$Fr_0 = Wr^1 \therefore F = \frac{Wr^1}{r_0} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and,

$$\mu_1 = \frac{F}{P} = \frac{r^1}{r_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Goodman's Oil-Testing Machine.—This machine (figs. 78 and 79) is a modification of the form used by Mr Tower, the correctness of whose experimental work has been amply confirmed by its use. A number of the experimental results obtained with this machine have already been given. It is thus described by Prof. Goodman:—

A is the journal on which the frictional resistance of the brass B is measured, it is tightly fitted into the cast-iron stirrup C, and the weights are suspended from it by the link D, which rests on the knife-edge E. The oil bath F is filled with oil, into which the bottom of the journal dips. A lubricator G is provided for siphon experiments. The temperature of the journal can be kept fairly constant by using the circulating water pipe H, the waste from which is carried away by the pipe J. The shaft is driven by the lathe chuck K, the revolutions of which are registered by the counter L. The temperature of the brass is registered by the thermometer M. The arm O carries the scale pan Q, which is suspended from the knife-edge S, the whole of which is counterbalanced by the weight N. The pointer P indicates when the arm is horizontal, the long arm of which is balanced by the small weight R.

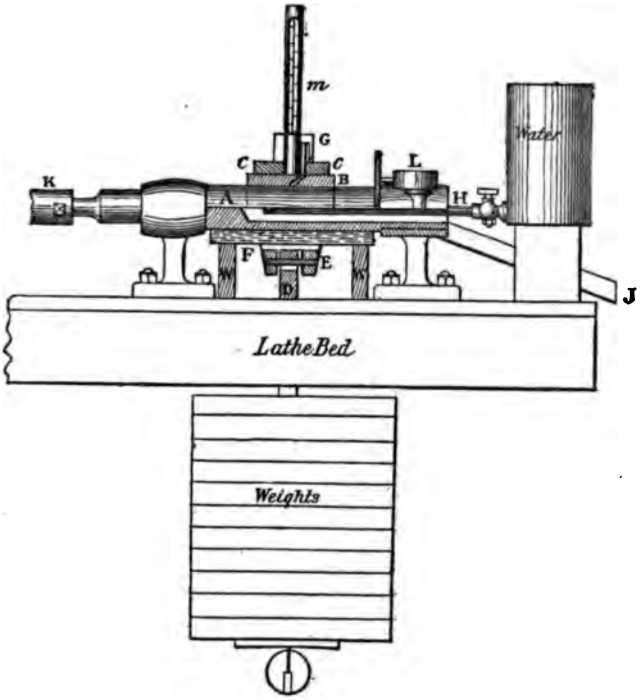

FIG. 78.

Disc and Collar Machines—*Suitability of, for Oil Testing.*—The wedging action of the lubricant, resulting from the different radii of the surfaces of cylindrical journals and the brasses which rest upon them, does not affect the lubrication of collar- or disc-shaped surfaces to any very great extent. On this account, the loads which such flat bearings will carry are about ⅛th part of those which may be put upon journals. Collar and disc lubrication mainly depends for its efficiency upon the oiliness or greasiness of the lubricant used. Such bearings would, therefore, seem to be well calculated to give good results in oil-testing machines. Of course they will always give comparatively high frictional resistances, and, therefore, must not be regarded as suitable for comparison with those obtained with the cylindrical bearings of actual working machines or machine tools. However, as the conditions which obtain in lubricated bearings become better understood, it seems likely that disc or collar machines, highly loaded and running at moderate speeds, will be more and more extensively used for oil-testing purposes.

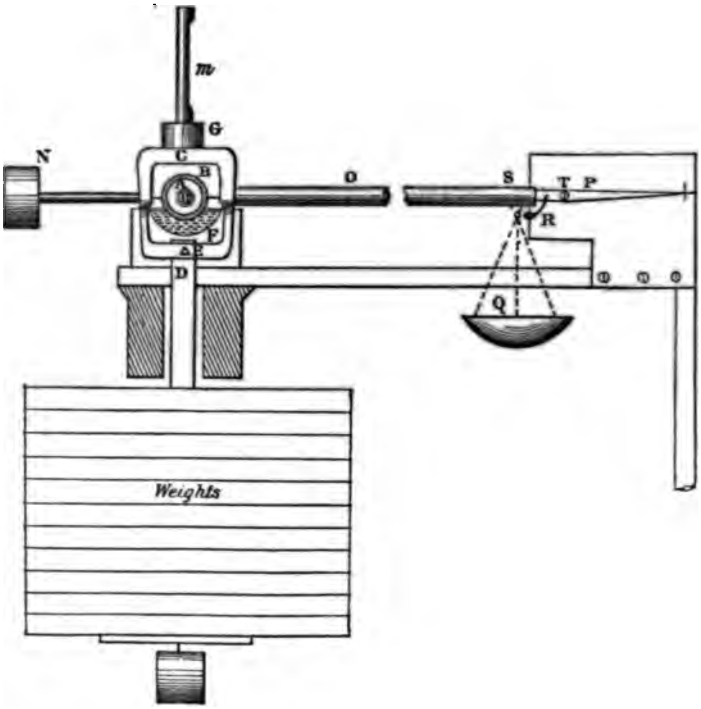

FIG. 79.

MacNaught's Testing Machine.—This, which is one of the earliest forms of disc oil-testers, is shewn in fig. 80. A vertical spindle A, driven by a pulley D, carries on its upper end a circular plate E.

Upon this plate rests a disc F, a projecting stud on which, when the disc is rotated by the friction between it and the rotating plate below, presses against a pin fixed on an arm attached to the weighted lever G H. A few drops of oil having been placed between the plate and disc, and the apparatus set in motion, the adjustable weight J is moved until a condition of equilibrium is established.

Woodbury's Oil-Testing Machine.—This machine is an improvement

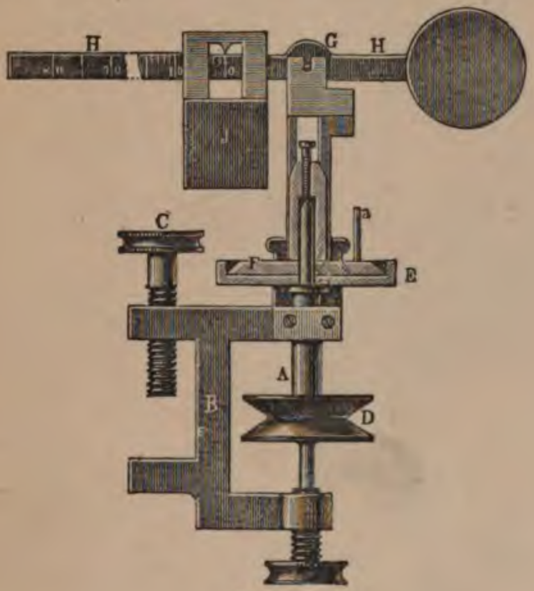

FIG. 80.

on that of MacNaught. The lower disc is fixed to the upper end of a vertical shaft to which the driving pulley is secured. The upper bearing surface is an annular ring placed somewhat eccentrically with the disc below, to secure uniform wear. The ring is hollow, is divided by a vertical partition into two passages through which water can be passed to control the temperature, and the sides and top are surrounded by a hood of hard india-rubber packed with eider-down. The load is applied by weights placed beneath the table and slung from a cross bar resting upon a vertical spindle, the thrust of which is transmitted to four points on the upper ring by a cross-shaped lever and central ball and socket joint. The bearings which carry the upper shaft can be rotated in different directions by means of pulleys, so as to reduce the frictional resistances. This arrangement allows the annular ring to rotate freely through several degrees and actuate a spring dynamometer which shews the frictional resistances, the cross beam, weights, etc., being free to move with it. The lubricant under trial is conducted, by a sight-feed arrangement, through the central opening in the upper ring to a recess in the centre of the lower disc. A counter indicates the number of revolutions made in any given time, and a thermometer shews the rise of temperature.

Deprez and Napoli's Testing Machine.—This machine, which is shewn in fig. 81, resembles Woodbury's machine in some respects. The load is applied by a lever and weight which forces three inclined bronze blocks, each having a surface of 10 square centimetres, into contact with a rotating disc below. The turning moment is measured by means of a pendulum, actuated by a steel band connected to the disc carrying the friction blocks S S S. An automatic record is drawn upon a sheet of paper stretched upon a small trolly set in motion by a pendulum, the pencil being fixed to a travelling arm.

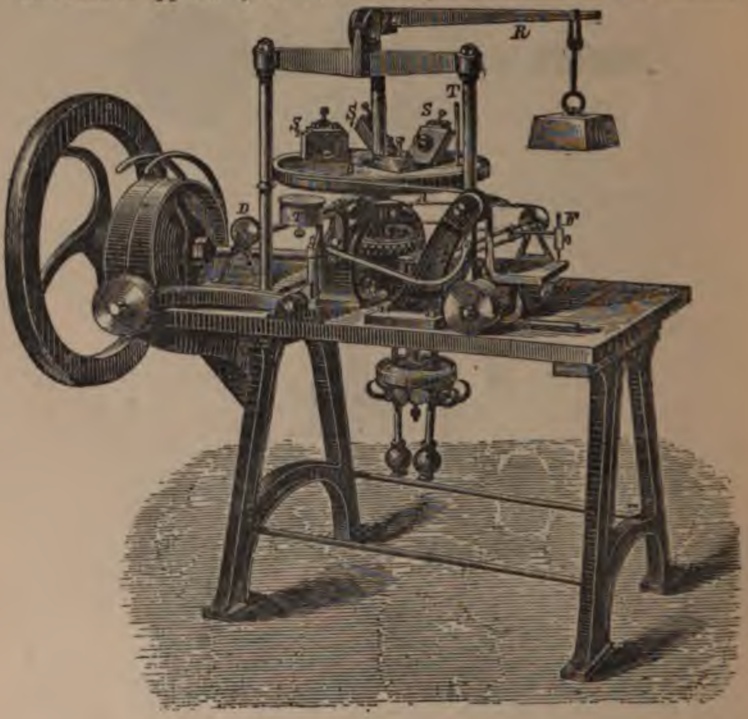

FIG. 81.

Tower's Disc and Collar Oil-Testing Machines. — Besides the machine for measuring the friction of journals, two other machines were designed and experimented with by Mr. Beauchamp Tower. One was for measuring disc- and the other collar-friction.

The apparatus used for measuring the friction of lubricated discs is shewn in figs. 82 and 105 (p. 381). The vertical shaft carrying the footstep gears into a horizontal shaft, the driving pulley on which can be changed to give the required speeds. A hard steel centre, secured to the bottom of the bearing B, rests upon a plunger fitting the cylinder P, whilst the vertical driving shaft is fitted at its upper end with a piston T of the same diameter as that of the cylinder P. By varying the pressure of the oil, which is supplied by a hand-pump with air vessel, the pressure upon the ram can be varied so as to give any desired load upon the contact surfaces. Two radial grooves in the bearing, shewn on a larger scale in fig. 105, pass from the centre of the bearing face to within a short distance of its circumference, and the motion causes the lubricant to flow out at its periphery into the

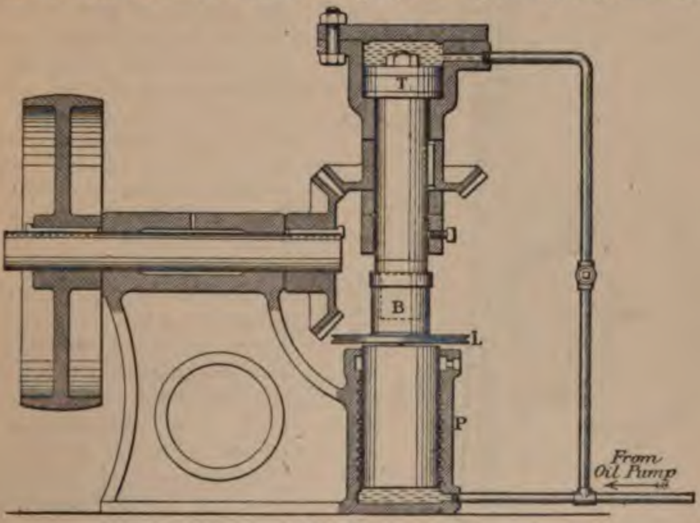

FIG. 82.

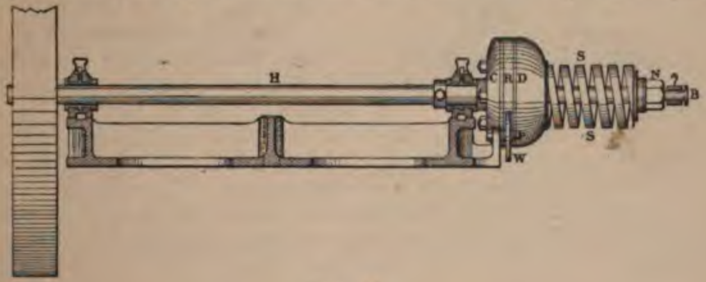

FIG. 83.

annular space surrounding B, from which it passes through a spout, and drops into the pipe, from which it again enters the bearing. A pulley L, actuating a spring, shews the frictional resistance of the surfaces.

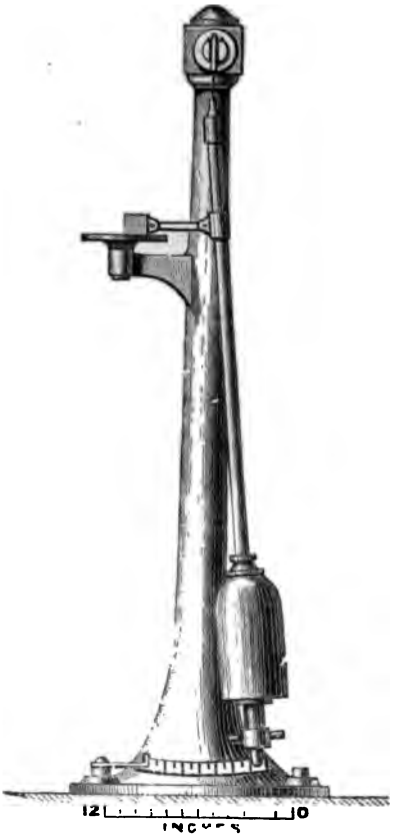

Fig. 84.

The machine shewn in fig. 83 was designed to measure the friction of a collar. The weight was applied by a delicately adjusted spring S, one end of which abutted against the front disc D, while the other end pressed against a nut N on a central bolt B connected with the disc C. The two discs rotating together, and pressing on the steel ring R, tended by friction to carry it with them, but were prevented from doing so by a horizontal lever attached to the ring, the friction between the ring and discs being measured by a spring-balance attached to the end of the lever. The methods of lubrication used, and the conditions under which the experiments with this machine were made, were not such as met with general approval, it being considered that the information gained by its use was not so complete as the machine was calculated to furnish.

Bailey's Pendulum Oil-Testing Machine.—This tester was designed for testing such oils as are suitable for watches, clocks, and other small machines. The small brass disc linked to the pendulum (fig. 84) rests upon a horizontal plate. When the pendulum is set in motion the friction of the disc slowly brings it to rest, the friction of the rubbing surfaces being estimated from the time it takes to do this.

CHAPTER X.

THE DESIGN AND LUBRICATION OF BEARINGS.

Forms of Bearing Surfaces.—Bearings are the surfaces of contact between the moving parts and the frame of a machine, or of one moving part and another. They guide the motions of the pieces they carry, and their shapes depend on the nature of the motions required. When, for instance, the piece is required to move in a straight line, the bearing must be either plane or cylindrical, with the axis in the line of motion. On the other hand, rotating pieces must have surfaces accurately turned to figures of revolution.

The parts of moving pieces which are in contact with the bearings may be classified as slides, gudgeons, journals, bushes, pivots, and screws. We also have to deal with 'line' contact surfaces which, if they do not act as guides, yet have tangential motion.

Owing to the weight of the moving parts, or the stresses the machine has to transmit, the bearing surfaces are pressed together with considerable force. Consequently, not only must the moving parts and the frame of the machine be strong enough to bear the stresses to which they may be subjected, but the contact areas must be sufficiently large to prevent overheating and undue wear. To secure the required area of bearing, the rubbing surfaces are frequently made very long and narrow, whilst in other instances they are square, or approximately circular.

Nature of Surfaces in Contact.—Although it is true that, in the majority of instances, the selection of a suitable lubricant, and its proper method of application to the surfaces, are of paramount importance, it very frequently happens that the conditions of working are such that particular attention must be paid to the nature of the surfaces which are to work in contact, otherwise rapid wear will take place. Such wear may result from the fact either that the rubbing surfaces are exposed to the atmosphere and become dirty and gritty, or that the bearing surface is merely a line, or that the motion is too slow or too fast and the load heavy.

The possibility of maintaining a machine in good condition without the frequent renewal of parts, depends largely upon the care which has been exercised in designing it so as to secure the conditions under which perfect lubrication is obtained. When the conditions are such that perfect lubrication is impossible, care must be taken to make the rubbing surfaces of as durable a material as possible. To effect these objects under the diverse conditions of everyday practice, a large number of devices have been introduced, a few of the principal of which we purpose describing.

Protection of Bearing Surfaces.—It is now becoming the practice, wherever possible, to carefully protect all rubbing surfaces by inclosing them in dust-proof cases, which shield them from grit and dirt. Too much attention cannot be paid to this point in the design of all kinds of machinery, but it is essential that the chamber in which the moving parts are placed should be fitted with openings, which admit of free access to all the bearings.

Chain and spur gear, especially, should be well protected. Cycles, for example, have all such parts made as dirt- and dust-proof as possible, and the bearing surfaces are thereby enabled to work freely on each other, and their durability is much increased.

Individual bearings, such as axle-boxes for railway vehicles, are also made dust-proof; for, now that oils which will not seriously gum or turn acid can be obtained, lubricants may be used over and over again, provided they are kept free from dust and dirt.

Materials and Lubricants for Bearing Surfaces.—Before the introduction of mineral oils for lubricating purposes, the necessity of paying considerable attention to the nature of the contact surfaces was not so great as now, for, as both animal and vegetable lubricants remain fairly viscous when heated, and possess the property of oiliness or greasiness very markedly, metallic surfaces, separated by fatty oils, unless subjected to excessive loads, seldom injure each other seriously. On the other hand, since the introduction of the less 'oily' mineral oils, it has been found more and more necessary to use the so-called 'antifriction metals' as bearing surfaces. Indeed, a study of the effects produced by varying the nature of the metallic or other surfaces in contact has, of late years, been forced upon the engineer by the conditions of running and the nature of the lubricants available, with the result that greater attention is now paid to this point in machine design. Of course the advantages gained by making the bearing surfaces of different materials were recognized at a very early date; but brasses and bronzes of various kinds, working against iron or steel, proved quite sufficient, as a rule, to prevent seizing and heating.

As, when two clean surfaces work against each other, the softer of the two (providing they do not seize) wears much more rapidly than the harder one, it is well to make that surface which is most easily and cheaply replaced of the softest material. The rubbing surfaces of a bearing are, on this account, removable pieces (steps or bushes), which are easily replaced by new ones.

Indeed it is not too much to say that the introduction of mineral oils, and the recognition of the true part played by viscosity in lubrication, have necessitated great alterations in the principles of design so far as the contact surfaces of machines are concerned; for mineral oils, although stable even when heated, and giving excellent results on properly designed bearings, are generally deficient in the power of maintaining lubricating films between bearing surfaces when the speeds are low, or when the faces are pressed together by heavy loads.

Exposed Rubbing Surfaces.—There are numerous instances in which rubbing surfaces cannot easily be protected from air, water, dust, etc., and in which the lubrication cannot but be imperfect. As a rule when this is the case, neither of the surfaces are made of a soft material, as grit, etc., may become imbedded in the surfaces of the metal and act as cutting tools. Various hard substances are brought into requisition for such purposes; for the load to be carried, the speed of rubbing, and the presence or absence of jars or knocks have all to be taken into account when selecting a suitable material. In some cases toughness, as well as hardness, is of importance, whilst in other cases a hard but comparatively brittle material will give the best results.

Hardening of Bearing Surfaces.—*Hard Steel Surfaces.*—In the case of line contact, such as occurs in the various forms of trip gear for Corliss engine valves, the best results are obtained with tempered steel faces, screwed, or otherwise secured, to softer metal supports. Such faces last well if reasonable care be taken to keep them free from grit, and to lubricate them well with a fairly viscous oil.

Hard steel surfaces having considerable contact areas, and which carry heavy loads, are, as a rule, made to work against softer materials. When two such hard surfaces have to work against each other, they must be very accurately fitted, and such provision made in the design as will admit of an equal distribution of the load, even if the parts should not run quite accurately together.

Low carbon steel, if used for shafting, cranks, journals, and the like, is very apt to give trouble, the metal being too soft to make good bearings. On this account, engine makers now order steel containing as much as 0·4 per cent. of carbon. With such material every care must be taken to insure thorough annealing, otherwise large masses will prove difficult to work and rather brittle.

In many instances, the conditions of work are such that efficient lubrication is impossible. For instance, parts of sewing machines and of watch and clock mechanism, knitting machines, and many other contrivances, such as machine gun mechanism, have to depend very largely for their durability upon the hardness of the bearing surfaces and their suitability for working in contact with each other. Many rubbing surfaces upon which the load is small are never really lubricated, for even the contamination film is rubbed off. In such instances, it is absolutely necessary that the materials used should be exceedingly [illegible] will not adhere firmly together, even when the surfaces are chemically clean.

It is now becoming more clearly recognised that solids possess properties which have been generally regarded as peculiar to liquids. Thus lead, when quite clean, is sticky, two pieces welding together upon being brought into contact. But not only do some solids easily weld together in the cold, they even diffuse into each other.

It will be seen from this how important it is to pay the most particular attention to the physical properties of the metals used for rubbing surfaces.

When it is necessary to make the surfaces as hard as can be obtained by the use of very high carbon tempered steel, the speed of rubbing is generally low. There is consequently a very small liberation of heat.

Burnished Bearings.—Lubricating films are so very thin that to allow of their proper formation the rubbing surfaces must be exceedingly true and smooth. To bring them into this condition before they are put to work burnishers are frequently used. The burnishing rolls are pressed firmly against the surface of the journal or other part and produce a very excellent rubbing surface. When the material used is wrought iron, steel, or even brass or bronze, the compression of the metal causes it to flow under the burnisher and become very much harder. Indeed the surface hardness produced may be comparable to that resulting from drawing wire through dies. Such a hard bright surface will wear better than an annealed one, and be less liable to [illegible].

[illegible] and Mild Steel.—Hard steel is too brittle for [illegible] parts are, therefore, made of case-hardened [illegible] of iron which have had their surfaces [illegible] by heating the metal for some hours in a [illegible] with bone-dust, leather and horn cuttings, with subsequent [illegible] in cold water. A very superficial hardening is [illegible] surface of the metal heated to redness, [illegible] and quenching in water. This case-hardening [illegible] wrought iron to open along seams, [illegible] the mass of metal. Wrought-iron journals of large [illegible], seldom case-hardened.

Where [illegible] hard surfaces are made use of for bearings, it is necessary [illegible] the case-hardened surfaces to insure [illegible] area.

[illegible] Surfaces.—For slide-blocks and slides, chilled cast-iron surfaces, [illegible] true, are even more suitable than those of steel or case-hardened iron. Here the hardening effect is produced by casting the fluid iron into massive metal moulds or 'chills,' the sides of which are previously coated with a clay wash to prevent the casting adhering to them. In this way the cast metal is rapidly cooled, the graphite is prevented from separating from the iron, and the chilled portion of the casting becomes extremely hard, and, if broken,

shews a silvery fracture. In the cooling process, however, the casting is much distorted. To remedy this, the pattern must be made of such a shape that the cooling effects shall draw the casting into the required form. To reduce the risk of fracture, it is customary to make chilled surfaces in loose pieces, which can be bolted to the frame of the machine or to its moving parts.

Estimation of Hardness.—Although we speak of bodies as being hard and soft, these are scarcely scientific terms, for the hardness of different substances measured in different ways is by no means always the same. For our purpose, hardness may be defined as the resistance offered to permanent plastic deformation. We must clearly distinguish between mere skin hardness and the hardness of the mass of the metal, for, exposure to air, etc., or mechanical and chemical treatment, will often harden the surfaces of even soft bodies considerably.

A series of experiments by Bottone; who measured the load necessary to produce a cut of definite depth, shew great differences in the hardness of different metals. In his scale of hardness, the diamond is taken at 3010. His determinations of the relative hardness of twenty metals are as follow :—

TABLE XCIII.—RELATIVE HARDNESS OF METALS.

Manganese,	1456	Gold,	979
Cobalt,	1450	Aluminium,	821
Nickel,	1410	Cadmium,	760
Iron,	1375	Magnesium,	726
Copper,	1360	Tin,	651
Palladium,	1200	Lead,	570
Platinum,	1107	Thallium,	565
Zinc,	1077	Calcium,	405
Silver,	990	Sodium,	400
Iridium,	984	Potassium,	230

Prof. Unwin has devised a method of measuring hardness by using a straight knife-edge as the indenting tool. Several series of observations of the indentations produced in $\frac{3}{8}$ inch bars of different metals with various loads were made, and for each metal a constant was deduced which is a measure of its hardness. It was found that the equation $C\,i = p^{1\cdot2}$ may be taken as the relation between the load and indentation, C being a constant giving the relative hardness of the metal tested, i the depth of the indentation in inches, and p the pressure in tons per inch width of knife-edge in contact with the bar.

Using this formula, Prof. Unwin obtained the following relative hardness of a number of metals :—

Cast steel, normal,	554·0
Brass No. 2,	246·0
Brass No 1,	221·0
Mild steel,	143·5
Copper, unannealed,	105·2

Aluminium alloy, cast	103·5
Copper, annealed	62·0
Aluminium, annealed	41·8
Zinc, cast	40·8
Lead, cast	4·2

The relative scales of hardness obtained by both the scratch method and the indentation method are said to be practically the same, but the scale obtained with the indentation method is a more open scale than with the scratch method, which remains to be described.

The scratch method is not suitable for very hard or brittle bodies, or for determining surface hardness. The latter may be best ascertained by the use of Turner's sclerometer (hardness measurer), a modified form of which, described by [illegible] and Bloxam,* is shewn in fig. 85.

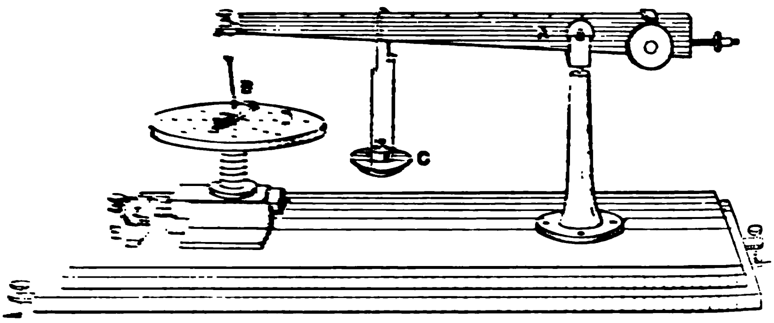

FIG. 85.—TURNER'S SCLEROMETER.

The graduated beam A swings on a pivot in a horizontal plane and also on knife-edges in a vertical plane. At the end remote from the knife-edges is a style B, shod with a diamond point. To prevent the style from chattering it is placed at an angle with the plane of the beam. A scale-pan C slides along the beam, which is graduated, and by this means a load varying from 1 to 100 grammes can be placed upon the diamond point. The piece to be tested is prepared with a polished surface free from scratches and is clamped on the rising table D. The diamond point is loaded with a known pressure and drawn across the polished clean surface. By means of the screw E the table is moved bodily a short distance—*e.g.*, $\frac{1}{50}$ inch—and another trial made with a different load. The load which just suffices to abrade the specimen is a measure of its surface hardness. The instrument is preferably used in conjunction with a low power microscope (1 inch objective) to view the scratches and decide which corresponds with the abrading load. The following table (Turner) shews the hardness of various materials, the figures being the load in grammes required to just scratch the specimen when tested by the sclerometer :—

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* *Engineering Chemistry*, vol. i. pp. 28-31.

Steatite,	1
Lead, commercial,	1
Tin,	2·5
Zinc, annealed,	6
Copper,	8
Softest iron,	15
Mild steel,	21
Tire steel,	20–24
Hard cast iron,	36
Hardest chilled iron,	72

Materials for Bearings.—*Cast-iron.*—Excellent bearing surfaces are made of unchilled cast-iron. The only objection that can be urged against this metal is that it is rather brittle, especially when heated by friction. It not only works well in contact with steel or wrought-iron, but also against itself. Even when heated it does not seize readily, the surfaces grinding to powder and remaining free to slide over each other so long as any solid material remains. On this account it answers well for steam cylinders, in which the lubrication is apt, at times, to be very imperfect. Loose pieces are not required, for the barrel and valve faces are merely machined portions of the casting.

The suitability of cast-iron for bearing surfaces arises, no doubt, in a great measure from the presence in the iron of particles of graphite and to its porous surface into which the lubricant insinuates itself. Sometimes powdered solids, such as plumbago, are used as lubricants for cast-iron surfaces, the powder being dusted upon the exposed portions of the rubbing surfaces.

Bronze.—In the majority of instances, the material of which a bearing is made must not only differ in melting-point and hardness from that of the surface against which it rubs, but it must also be sufficiently strong and tough to stand heavy blows and great stresses without fracture. Copper, although it possesses a high malleability, softness, ductility, toughness and tenacity, is not a suitable metal of which to make bearings, for it can only with difficulty be made to produce sound castings, and is too tough and close-grained to be easily shaped in a lathe. Copper is therefore alloyed or mixed with other metals, forming gun-metals, bronzes and brasses of various kinds. The metals added are generally tin and zinc, and occasionally lead, antimony, and iron.

Gun-metals are alloys of copper and tin in various proportions. Not only does the tin greatly increase the hardness of the alloy, but it makes it more fusible, and enables excellent castings to be obtained. Many of these mixtures are not uniform in texture, whitish spots of an alloy, rich in tin, being distributed throughout the mass. To insure an intimate mixture of the metals, bronze castings are frequently chilled either in the mould, or by immersion, when red-hot, in water. This rapid cooling prevents the segregation of the metals, or alloys thereof, much in the same way as chilling prevents the carbon in cast-iron from separating as graphite.

Ordinary bronzes contain zinc as well as tin, the presence of the former metal much facilitating the casting process. Tin confers hardness upon the alloy, thus rendering the mixture less liable to seize and injure the bearing surfaces when overheated. The tin and zinc also prevent the bronze from tearing while being machined, and enable it to be filed and machined with ease to the required shapes. When the copper reaches 80 per cent., the alloys are often capable of being forged at a red heat. Gun-metals for bearings sometimes contain as much as 18 per cent. of tin, and being rather softer than wrought iron, or mild steel, wear more rapidly. On this account, except when the loads are very heavy, they are suitable for steps upon which rotating pieces are supported.

The addition of phosphorus, in small quantity, to copper and tin appears to have a good effect upon the alloy, and greatly increases its load-carrying power. For pinions, and valves, about 7 per cent. of tin is added to the copper, and 0·1 per cent. of phosphorus; but when great strength and hardness are required, 8 or 9 per cent. of tin is added, and about 1 per cent. phosphorus. Phosphor-bronze is much used for axle-bearings, slide-valves, bushes, cog-wheels and all parts of machinery which are subject to much friction. Although the proportion of phosphorus present is small, it exerts a very beneficial effect upon the mixture. Its action, however, rather results from a refining influence than to the formation of a phosphorus compound.

Manganese bronzes, both with and without zinc, are made by introducing a proportion of ferromanganese into bronze or brass. A variety free from zinc, which has great strength and toughness, has been used for very large bearings. Great strength and toughness has also been secured by adding aluminium in small proportion.

Bronzes, of various qualities, are very extensively used for bearings, working both with and without lubricants. In many cases, such as where the alloy works against the bearings of cast-iron rolls, the heat resulting from excessive friction is prevented from raising the temperature unduly by a stream of water. Bronzes are also used for bearing surfaces working against steel and iron, when the load is not excessive and fluid lubricants are used, also for steam engine slide-valves working against cast-iron surfaces, especially when the load resulting from the steam pressure is great. Bronze and cast-iron surfaces are very hard and unyielding, and, unless the surfaces are very true and run accurately upon each other, they are apt to bind heavily in places and cause over-heating, more especially if non-oily or non-greasy lubricants are used.

When zinc is substituted for tin, the alloy is a brass. For bearing surfaces brass is by no means so good as bronze. Nevertheless, as zinc is much cheaper than tin, and brasses are less expensive than bronzes, they are much used in cases where, owing to the loads being light, strength and ductility are of secondary importance.

In Table XCIV. th[illegible]ntage composition is given of several of lloys used for bearings. They are arranged according to the ion of copper which they contain.

XCIV.—Percentage Composition of Machine Bearings, &c.

Description.	Copper.	Tin.	Zinc.	Other Metals.
heels,	91·0	...	9·0	...
tric rings,	90·0	7·7	2·3	...
hard axle bearings,	89·0	...	11·0	...
balls,	87·0	12·0	...	Antimony 1
otive axle bearings,	86·0	...	14·0	...
ng boxes,	86·0	11·0	3·0	...
ary bearings,	84·5	13·3	2·2	...
y bearings,	84·0	12·0	4·0	...
s,	84·0	7·0	9·0	...
rings,	84·0	2·9	8·3	Lead 4·8
ary bearings,	83·6	12·6	3·8	...
nical instruments,	82·0	13·0	5·0	...
otive axle bearings,	82·0	10·0	8·0	...
h railway carriage rings,	82·0	18·0	...	...
axle bearings,	82·0	16·0	2·0	...
-cock ways,	81·0	...	19·0	...
ulic pumps,	81·0	...	19·0	...
ller shaft-liners,	80·0	5·4	14·6	...
whistles,	80·0	17·0	3·0	...
y bearings,	77·0	9·0	14·0	...
e wheel pins,	76·8	17·4	5·8	...
bearings,	75·0	4·0	21·0	...
rately hard axle bearings,	70·0	22·0	8·0	...
tric rings,	66·0	15·5	18·5	...
ller boxes,	57·0	14·0	29·0	...
metal (pumps),	55·0	6·0	22·5	Iron 16·5
s,	34·0	50·0	16·0	...

te-metal.—White-metals, sometimes known as white brasses, w coming largely into use, owing to the comparative ease with they can be scraped down to form smooth and polished sur- nd the satisfactory way in which by their use the friction is w under conditions which do not admit of perfect lubrication. earing surfaces are also cheaper than those made of bronze, for tal removed by wear can be replaced at very small cost, and t destroying the bronze, brass, or cast-iron step of which it the rubbing surface. The use of white-metal also, in many nables mineral lubricants deficient in oiliness to be used in f the more costly fatty oils. The mineral oil of Pechilbronn, ance, has been found very satisfactory when used in connection with white-metal on the Eastern Railway of France,* where it was tried for high-speed railway vehicles. Not only was a great pecuniary saving effected by using this oil as a lubricant in conjunction with white-metal, but the number of heated axles was reduced in the proportion of about 7 to 1.

Anti-friction, or white metals, are white alloys of copper, tin, antimony, lead, zinc, etc. It is seldom that more than three of these metals are used in any one mixture. The general practice is to cast recesses in the surfaces of bearings of the ordinary form, fill them with the white alloy, and then tool and scrape the surface so as to fit the shaft or journal they are to work upon. Generally speaking, the bearing block or 'brass' is made of a tough bronze; for marine work, however, cast-iron is now largely used. The white-metal is let into the surface in longitudinal or diagonal strips which stand a little 'proud' of the cast-iron. This gives the shaft a chance of quickly producing a true smooth-bearing surface, which, as it wears, allows the shaft to slowly put a good face on the cast-iron as well. The initial process of producing a good face should be effected under easy conditions of running, so as to avoid over-heating. Being porous, the cast-iron surface is easily contaminated by small flakes of white-metal, which, to some extent, act as lubricants. If, from any cause, a bearing of this description should become over-heated and the white-metal melted away, then the surfaces of the cast-iron ribs carry the load, and if the bearing be kept cool by directing a stream of cold water upon it, the engine need not be stopped until a favourable opportunity offers.

To ensure the adherence of the white-metal to the bearing, the brass or bronze surface should be well cleaned, washed with alcohol, powdered with salammoniac, heated, and then tinned.

As white-metals liquefy at about 440° to 480° F., they may be melted in ordinary ladles and run directly into the recesses prepared for them, the journal or shaft side of the mould being outlined by a suitable loose iron block. As some of these alloys do not adhere very well to the walls of the recesses prepared for them, the supporting edges of the latter should be bevelled in such a way that the soft alloy is mechanically held in position.

Some of the component metals being volatile at comparatively low temperatures, it is well not to heat the mixture more than is necessary to properly liquefy it. Care should also be exercised not to allow dross or other foreign material to get into the mould.

Table XCV. gives a list of some of the white-metals which have been introduced.

According to Dewrance, very little lead or zinc should be contained in white-metals which have to be lubricated with oils containing free fatty acids, as these acids form soaps very readily with the two metals named, and therefore corrode badly. Tin is not attacked so readily, and the safer plan is to use an alloy composed principally of this metal.

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* *Revue Generale des Chemins de Fer*, April 1885, p. 216.

ght be expected from the great variations in their composition,
etals vary greatly in the extent to which they reduce the
t of friction, and also in their toughness and hardness. The
ieties when clean, and working against iron or steel at
gly low speeds, give high coefficients of friction, but the heat

BLE XCV.—PERCENTAGE COMPOSITION OF WHITE-METALS.

Description.	Cu.	Sn.	Sb.	Zn.	Pb.	
ce's locomotive metal,	22·2	33·3	44·4	...	...	...
carriage bearings,	22·0	67·0	11·0	...	...	...
son's alloy,	19·0	31·0	...	19·0	...	Fe 31
y bearings,	12·0	...	...	...	88·0	...
"	10·0	...	10·0	...	80·0	...
earings,	9·0	73·0	18·0	...	...	...
n bearings,	8·0	2·0	2·0	88·0	...	...
acking,	7·78	88·16	3·51	...	2·5	...
navy,	7·5	85·0	7·5	...	...	...
od packing,	7·5	86·5	3·5	...	2·5	...
navy,	7·0	7·5	...	78·5	7·0	...
earings,	7·0	76·	17·0	...	...	...
bearings,	6·0	87·0	7·0	...	...	...
tion metal,	6·0	14·0	...	80·0	...	...
n's metal,	6·0	88·0	...	...	...	Hg 6
s metal,	5·5	14·5	...	80·0	...	...
y bearings,	5·3	84·2	10·5	...	...	...
s alloy,	5·0	85·0	10·0	...	...	...
er bush,	5·0	26·0	...	69·0	...	...
ry bearings,	5·0	81·0	14·0	...	...	...
"	5·0	81·0	...	...	14·0	...
earings,	4·0	12·0	82·0	2·0	...	...
s metal,	4·0	82·0	14·0	...	...	...
bearings,	2·0	90·0	8·0	...	...	...
s metal,	1·5	45·5	13·0	...	40·0	...
alloy for pivots,	...	46·0	12·0	...	42·0	...
r's lining alloy,	...	18·0	2·5	75·0	4·5	...
y bearings,	...	5·0	15·0	...	80·0	...
ia metal,	...	...	21·0	...	78·0	Fe 1
s metal,	...	58·5	2·0	39·5	...	...
railway carriage,	...	38·0	25·0	...	37·0	...

l is so small and the adhesion of the surfaces so slight that
y is done to the rubbing surfaces. Should the pressure be
heavy, the metal is merely flaked off, or flattened, the load
and the surface burnished. On this account, white-metal
are indispensable for certain purposes; as, for instance, when
ft resting on the bearing cannot be made to run quite
ly.

As an illustration of the extent to which these soft metals reduce the friction when working on hard steel at ordinary speeds without unguents, we may instance the case of Magnolia metal. Professor R. H. Smith states that when running with pure water instead of a true unguent the coefficient is as low as ·03, the load being about 400 lbs. per square inch. With brass, under similar conditions, the friction is five times as great.

When the pressures per square inch are great, or the bearings are subjected to severe shocks, very hard mixtures are required. Such an alloy is Dewrance's 'Wheel Brand,' which stands a high compression test. Soft metals under such circumstances suffer severely their surfaces being rubbed off in flakes.

It will be noticed that most of the white-metals given in Table XCV. page 351 contain antimony. This metal has the important property of preventing the mass from shrinking much upon solidification, or of actually causing it to expand and therefore fill the cavity in which it is run. When present in the alloy in large proportion, it makes the mixture very hard and brittle. The brand of Dewrance's metal above referred to, for instance, which contains a large percentage of antimony, must be well supported, and must not be hammered after having been poured into the recess in the bearing. The hardening effect is, however, generally obtained by the use of tin and zinc, toughness by copper, and softness by lead. Zinc does not alloy with lead in all proportions, and it will be found that these metals are seldom present together in alloys. Tin, on the other hand, alloys well with both copper and zinc.

The high pressures, and, consequently, high temperatures, at which steam engines now work renders hemp, or other fibrous packing, unsuitable for piston rod glands, for the fibre is charred by the heat and the packing loses its firmness. Metallic packings are, in consequence, largely superseding vegetable fibre. The following is an analysis of a packing which stood well in the piston rod gland of an express locomotive:—

Lead.	Tin.	Antimony.	Copper.
2·5	88·18	3·51	7·78

When lead is used in place of tin the alloy is too soft, and the metal is forced out of the gland in flakes.

Sometimes such alloys are placed in the stuffing-boxes, either in the form of rings or solid segments, or they are fixed as segments in special frames which are free to move laterally so that no undue pressure shall be put upon the rubbing faces if the piston rod should not run quite true. Such packings require regular and good lubrication, and the piston rods must be kept truly cylindrical, or the metal will shell out of the gland and steam escape.

White-metals called 'Tandem Anti-Friction Alloys' are supplied, of three qualities. They vary in hardness very considerably, and it is recommended that they be used as follows:—

Hard metal, A.—For heaviest pressure and medium speed, or for heavy pressure and high speed, such as main bearings of marine engines, boxes of large steamship crank-shafts, locomotive axle bearings, bearings for rolling mills, dynamos, large wood-working, centrifugal and spinning machinery, emery wheels, etc.

Medium metal, B.—For heavy pressure and medium speed, or medium pressure and high speed, such as axle-boxes of railway wagons, tramcars, bearings of steam, gas, and oil engines, medium crank-shafts, rolling mills, grinding and pumping machinery, and all kinds of journals and ordinary shafting.

Soft metal, C.—For medium pressure and high speed, or for low pressure and highest speed, such as the bearings of light machinery and shafting, for steamship tunnel shafts of all sizes, axle bearings of field, transport, and tipping lorries, for cement, clay and brick-works machinery, and also for bearings of high speed machinery.

Aluminium.—Aluminium, owing to its lightness, is now to some extent supplanting brass and German silver for many small instruments, such as microscopes and opera glasses. However, the metal is not only difficult to tool and work, but surfaces of it will not slide freely upon each other, even when the load is small. When two aluminium pieces have to work together, a thin plate of steel is often secured to the face of one of them, upon which the opposing aluminium face slides freely, and with a very small amount of lubrication.

Wood and Hide.—In spur and bevelled gear we have to deal with line friction. Here one set of teeth in a pair of wheels working together is often made of some hard and dense wood, such as crab-tree, hornbeam, locust or beech, fitted into an iron frame, or centre, in such a way that the teeth can be taken out and replaced with new ones when much worn. Box, beech, holly, elm, maple, oak, hickory, canewood, snakewood and lignum vitæ are also much in request for shaft bearings, etc. Of these, lignum vitæ, which will sustain very great pressures without abrasion, is, perhaps, the most valuable, more especially as it works well under water. Such bearings as those of stern frame blocks and the gland in the ship's side to keep the water from entering, have this wood let into grooves cut into bushes of bronze. The strips thus let in stand somewhat above the metallic surface, so as to allow of a free circulation of water, and the grain is placed at right angles to the rubbing surface of the shaft. Lignum vitæ, also, is sometimes used for hydraulic valve faces, pivots, etc. The circumstance that it works well under water is no doubt due to the fact that throughout the cells forming the woody structure are distributed resinous substances which act as lubricants, and, however much it may be abraded, the surface of the wood has always a smaller superficial tension than has water, and therefore is always separated from the metal by a lubricant.

Rhinoceros hide is also largely used for gear wheels, as it wears well with small loads and runs silently.

Other Non-metallic Materials.—In the case of watches and very light, continuously running machinery, which cannot be regularly lubricated, hard steel pins running upon agate or jewelled bearings give the best results.

Even for large shafts, stone bearings are occasionally adopted. The natural stones suitable for this purpose are those which are wholly free from grittiness, and somewhat inferior in hardness to iron. Gypsum, pure clay slate, pure compact limestone, marble, and silicate of magnesia or soapstone (the last being the best) are those in most general use. Many soft rocks, such as sandstone, sandy limestones, and slates are not suitable, as they contain crystals of quartz—a hard mineral which scratches and grinds down even the hardest steel. A non-metallic material for bearings, called 'adamas,' consists of silicate of magnesia, ground, calcined, moulded by hydraulic pressure into blocks of suitable figures, and baked. The advantages to be gained from a lubrication point of view from the use of silicate of magnesia result from its combining a certain greasiness of surface with a degree of hardness sufficient to secure the requisite durability.

Several other mixtures of solids have been introduced which, it is claimed, run well on iron or steel without the use of any liquid lubricant whatever. They almost all contain graphite, mixed with some binding material.

At present it is only where, for some reason or other, oil or other lubricant is objectionable that such anti-friction materials are used, well designed and properly lubricated surfaces having proved more reliable and economical.

A solid bearing for shafts, etc., called 'carboid,' has lately been introduced by Mr. Killingworth Hedges. It is said to consist of powdered carbon mixed with a certain proportion of steatite, with the twofold object of consolidating the friable carbon and decreasing the friction. The 'carboid,' which may be fixed to the rough surface of a casting by a special cement, has been used for machinery for fine fabrics which oil would injure, for the bearings of steam-heated cylinders, and also for such bearings as cannot easily be lubricated. Prof. Unwin, who determined its friction coefficient, found that it followed somewhat closely the laws of solid friction.

Asbestos is also largely used as an anti-friction packing for taps and valves. It may be compressed until it becomes dense and hard, and capable of carrying a very considerable load, yet owing to its fibrous nature it holds together and forms a good smooth-bearing surface.

The Lubrication of Bearings.—*Friction and Speed.*—In the chapter on 'The Theory of Lubrication,' the effect of speed upon the coefficient of friction has been dealt with at some length. It was there shewn that both in the case of cylindrical and flat surfaces, when the speed exceeds about 10 feet per minute, and the lubrication is good, the resistance offered to the relative motion of opposing surfaces, owing to the viscosity of the intervening lubricant, is approximately proportional to the square root of the speed. At lower velocities, however, the frictional resistance follows quite different laws.

Although the conditions obtaining when the load is small (10 lbs. per square inch in the case of plane surfaces and 50 lbs. when the bearing is cylindrical) are interesting from a theoretical point of view, such loads are seldom used in practice except with very high speeds. We may therefore omit consideration of them here, and merely deal with such loads as have to be placed upon ordinary bearings, *i.e.*, those which exceed 40 lbs. per square inch in the case of plane surfaces and 100 lbs. for journals.

When we have to deal with well lubricated surfaces and ordinary loads, the coefficient of friction of rest is slightly less, to judge by such experiments as are available, than that of very slow motion, but with increasing speed a maximum is soon reached, beyond which the coefficient of friction rapidly decreases as the speed rises, until between 10 and 100 feet per minute is reached. At about 10 feet per minute, if the lubrication be good, it should be at a minimum. Diagram (fig. 24), page 60, has been drawn to shew the variation of the coefficient of friction with change of speed.

Slow-Speed Lubrication.—The oil films remaining between surfaces which have been pressed together, without tangential motion, for some time, are merely superficial tension films. They are in all cases exceedingly thin. Indeed, so thin are they that the minute irregularities of even polished surfaces are enabled to engage in each other to some extent. The greater the thickness of the surface film separating the solids, the greater the greasiness of the lubricant is said to be. A soap film, for instance, which has considerable greasiness, probably has a thickness somewhat exceeding ten millionths of a millimetre, and is stable in a humid atmosphere.

Our knowledge of the thickness of lubricating films, when they separate solid bodies, is really very incomplete; but that they are extremely thin, especially in the case of mineral oils, is proved by the fact that there is always considerable friction between even well-polished surfaces at extremely low speeds.

As, at very low speeds, the oil film is not sufficiently thick to keep the surfaces apart, they abrade each other somewhat, and when this is the normal condition of working, they must be made of metals which do not easily seize or weld together. In such cases the lowest coefficient is obtained by the use of fatty oils, which are generally mixed with mineral oils.

High-Speed Lubrication.—It has been shewn that when the speed of rubbing is considerable, and the load not too heavy, the manner in which the friction varies with changes of load, speed, and viscosity is such as to prove that it is then wholly due to the viscous resistance offered by the lubricant itself to motion, and is unaffected by the nature of the metals forming the rubbing surfaces.

[illegible] by a thickening of the [illegible] explained. As the effect, [illegible] we will illustrate the case by [illegible] plate is [illegible] with a [illegible] another face plate [illegible] the film is a thick [illegible] with the greatest ease. [illegible] between the surfaces [illegible] if the upper plate be [illegible] together and [illegible] it is clear that the [illegible] frictional resistance, and [illegible]

[illegible] cylindrical, are [illegible] is freely in[illegible] between them which reduces friction.

[illegible] therefore, to design his [illegible] and have as small a viscosity [illegible] the frictional resistance [illegible]

[illegible] we notice, results [illegible] show that the [illegible] is the [illegible]

[illegible]

[illegible] work. The [illegible] a low coefficient of [illegible]

[illegible] ed that not only have simple means been devised for supplying the lubricant in such a manner that the friction is reduced to a minimum, and that at the same time lubricants can be used over and over again and not wasted, the sooner the old unsatisfactory methods will disappear.

It should be clearly understood that the possibility of making practical use of such devices as will give results comparable with those obtained by Mr. Beauchamp Tower dates from the introduction of mineral oils and of non-acid fatty oils blended with them.

The original objection to *reservoir* bearings was that they required, in the first instance, a large supply of oil, which soon became viscid and useless by oxidation, etc., and that the reservoirs had to be frequently recharged.

This objection can no longer be considered valid, for good oils may now be obtained, a single charge of which can be allowed to work continuously for ten or twelve months without becoming objectionably viscid or acid.

The pressure films produced by the trapping of the lubricant when the supply is good are very considerably thicker than superficial tension films. In a particular instance, by an electrical contact method, Prof. J. Goodman found that a lubricating film had a thickness of one five-thousandth part of an inch, whilst Prof. Osborne Reynolds, from the friction of a particular bearing, estimated it to vary, in different places, from ·00077 to ·000375 inch in thickness (·0195 to ·0095 mm.).

In the chapter on 'The Theory of Lubrication,' the manner in which this film forms and thickens as the speed increases has been as fully considered as is possible without the introduction of advanced mathematical methods.

As previously pointed out, the importance of securing perfect lubrication has become more and more recognized since the classical experiments of Mr. Beauchamp Tower on the friction of lubricated surfaces were made. He shewed that the methods of applying the lubricant to the bearing in common use are often very imperfect, and not only lead to great waste of oil, but fail to allow the bearings to make the best of what they do get.

As is almost always the case with improvements designed to give increased economy, the introduction of better designed bearings and lubricating arrangements has been comparatively slow, for, as we shall find, there are mechanical difficulties to be overcome before, in all cases, the best results can be obtained, and the improved bearings are not always the cheapest or the simplest.

Then, again, the designs of bearing in common use, and the methods of lubrication adopted, have been the result of experimental practice which did not take much note of the actual frictional resistances met with, except when they were so great that serious heating was caused. Unscientific methods have consequently been largely followed, a cheap rather than an economical bearing being aimed at.

But it is certain that in the future the engineer will not be content with a bearing simply because it does not run hot and give trouble.

His object, as we have said, will be to reduce the friction and wear to a minimum, and to enable the power of his motor to be expended upon the work in hand rather than in overcoming avoidable resistances.

Even at the risk of appearing to emphasise too strongly the value of the many new designs which have been introduced for securing perfect lubrication, we shall illustrate some of the best and most largely used of them for the purpose of shewing the direction in which design is now moving. In the immediate future there is every reason to expect that many improvements in detail will be introduced, and instead of the design of the rubbing surfaces of a machine and the method of application of the lubricant being regarded as of comparatively little moment, they will receive their proper share of attention by the draughtsman. Steam and other motors, etc., will then be less likely to give trouble, owing to overheated or damaged bearings, than is now the case.

Oil Spray Chambers.—To secure the advantages of good lubrication as well as to keep out grit and dirt, many kinds of mechanism are now inclosed completely in cases containing the lubricant, which is thrown about by the moving parts, drenching all the exposed rubbing surfaces, and freely entering the oil-ways provided. In this way not only is the oil used over and over again, but perfect lubrication is secured, and, as previously pointed out, particles of grit and dirt are prevented from mixing with the oil and grinding away the rubbing surfaces.

The central-valve vertical engines of Messrs. Willans & Robinson have the whole of the moving parts inclosed in this way, and perfect lubrication is secured for all parts. The bed-plate forms a reservoir in which is placed castor or pure mineral oil, and water. At each revolution of the crank the lubricant is thrown about the upper portion of the chamber, lubricating the connecting rod ends, valve-gear, main bearings, etc. These engines may therefore be allowed to run with full load, and without a single stop, for more than a month at a time, for the wear is exceedingly small, and all the parts can be kept well supplied with oil.

Oil Pressure Film.—Given a good supply of a lubricant of proper quality applied at the proper place, we have a layer of oil trapped between the rubbing surfaces and completely separating them. Upon this film rests the load. The oil, therefore, is under very considerable pressure towards the centre of the bearing surface, but as we approach the edges, the pressure falls off, and reaches zero at the margin. This is no theoretical assumption, but a fact which Mr. Beauchamp Tower discovered by perforating the brass of a journal, and connecting to the hole a pressure gauge.

As the load is completely oil-borne, the distribution of pressure in the film depends upon the direction in which the load acts. The formation of the film, or pad of oil, results entirely from the viscous properties of the lubricant, as also does the friction.

Positions for Oil-ways.—When the speed of rubbing is slow, the lubricant is not trapped between the surfaces to any great extent, and does not form a thick sustaining film. In such cases, a lubricant possessing the property of oiliness or greasiness, rather than viscosity, is necessary, fatty oils giving the best results.

The lubricant is then kept between the surfaces because the oil or grease films powerfully resist rupture. Oil-ways, therefore, may be cut along those parts of the faces which are being forcibly pressed together, and can be made of such lengths, and extend in such directions, that owing to the close fit of the parts they will retain the oil fed to them. This cannot, however, be done with advantage when the speed of running is high and the lubrication 'perfect,' for oil-ways cut along faces to the edges, or from holes drilled where the pressure film should be, allow the oil to escape, and the surfaces then close together.

When the lubrication is 'imperfect,' the speed of running being only moderate and the journal of large diameter, it is often very difficult to keep the bearing cool, even if substantial fatty oils are used. In such cases, grooves are often made along the rubbing surface of the journal, and sometimes mere flat surfaces, of small width, are cut on their cylindrical surfaces. At other times, spiral grooves are cut round the surface of the journal, or, perhaps, several short grooves are cut at different points of the circumference. These grooves carry the lubricant between the rubbing surfaces, and the latter, therefore, are prevented from becoming dry.

Mr. C. E. Hefford,* R.N., has found that such a flat surface filed about 22° on the 'idle side' of the crank pin of an engine which always rotates in the same direction gives good results.

Such devices, however, except when the speeds are low, only serve to remedy the evils which result from imperfect lubrication, and should not be used in cases where the conditions are suitable for securing 'perfect' lubrication.

In the case of fixed machinery, the moving parts, in the majority of instances, rest upon the bearings, and run at speeds which admit of perfect lubrication. The lubricants in these cases can be supplied through holes and grooves cut in the cap of the bearing, for the pressure film or pad is on the lower brass. On the other hand, the axle bearings of railway vehicles rest upon the journal, and the lubricant should be supplied at the bottom or sides. Grooves in the top brasses allow the lubricant to escape, undue wear takes place, and the bearings are liable to run hot. Vertical engine main bearings are often subject to forces which tend to lift the shaft from its seat, and force it against the bottom and top brasses alternately. In this case we require a pressure film on the top as well as the bottom brass, and no grooves should be cut in either of them. The lubricant, under such circumstances, must be applied at both sides of the bearing.

In all bearings, the oil is intruded along the 'on' edge of the brass, and is expelled along the other three sides. Fig. 86 shews a plan of such a surface, and the arrows indicate, roughly, the paths of the oil across it. A portion of the oil escapes at the sides, the quantity being large when the film is thick and the lubrication good, and if some means be not devised for causing the oil thus expelled to return to the source of supply, it will be thrown about and wasted. In the majority of modern bearings guards are cast at the ends of the pedestal, and the oil, as it is thrown into them from the collars on the shaft, flows into a reservoir below the axle.

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* *The Practical Engineer*, 1st October 1897, p. 331.

Another plan (fig. 87) for preventing the expulsion of the oil at the ends is to cut oil-ways near the ends of the bearing, and, by

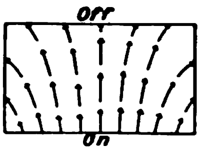

Fig. 86.

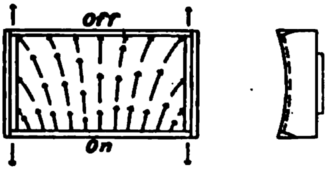

Fig. 87.

bevelling the brass, to provide grooves along the edge to distribute the lubricant along the journal face. If possible, all grooves in the brasses should be avoided, for dirt is apt to collect in them and fill them up.

Mr. Beauchamp Tower's experiments on the frictional resistance and loads carried by bearings with different methods of lubrication may be recounted here with advantage, as they shew in a very striking manner how important it is to cut the oil-ways of bearings in proper positions. Several methods of oiling were tested by him.

When the lubricant was supplied through a hole drilled in the crown of a brass (fig. 88) which rested upon a journal, and was distributed by means of a groove parallel to the axis of the brass and extending nearly to the ends of the bearing, it was found that the journal would not run cool when the load exceeded 100 lbs. per square inch. It appeared that the hole and groove being in the centre of pressure of the brass allowed the supporting oil film to escape. This view was confirmed by filling up the hole with the lubricant and then easing the weight off the journal for an instant. This allowed the oil to sink down the hole and lubricate the journal, but, immediately, the load was again allowed to pass upon the journal, the oil rose in the hole to its former level and the journal became dry, thus shewing that this arrangement of hole and groove, instead of being a means of lubricating the journal, was a most effectual means for collecting and removing all oil from it.

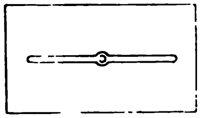

Fig. 88.

In practice, greater loads are carried with this faulty system of lubrication than these experiments would seem to indicate the possibility of. This, no doubt, results from the vibrations and side-play of the axle-box on the journal, and also to the imperfect fit of the brass, which allows the oil to get out of the groove and wet the journal. When the brass is a very good fit and the oil cannot thus escape, the bearings heat and give trouble. Small grooves, however, cut from the end of the oil-way to the end of the brass will often put matters right, for the lubricant can then escape at the ends and reach the journal by a circuitous path.

As the centre of the brass was obviously the wrong place to introduce the oil, Mr. Tower resolved to apply it to the sides, where two grooves were accordingly made. They were cut parallel to the axis of the journal, as shewn in fig. 89, and extended nearly to the ends of the brass. With this arrangement the bearing did not seize until the load reached 380 lbs. per square inch.

The arrangement sometimes used for locomotive axles was also tested. The oil was introduced through two holes, one near each end of the brass, from each of which ran a curved groove, as shewn in the plan, fig. 90.

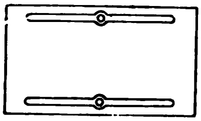

FIG. 89.

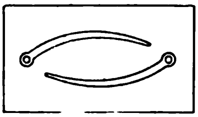

FIG. 90.

This brass refused to take its oil or run cool when the load exceeded 178 lbs. per square inch.

Pad Lubrication.—Having tested siphon lubrication with oil-ways of various kinds, Mr. Beauchamp Tower then experimented with brasses which had no oil-ways cut in them, the lubricant being supplied by pads pressed against the undersides of the journals. Although the oil was only supplied to the pads by capillary action, and the journals were only just oily to the touch, they carried loads of from 550 to 580 lbs. per square inch. The frictional resistance was also exceedingly small.

Woollen, or felt pads, kept moistened with oil and pressed against the journal, are now largely used. Journals or shafts should be kept uniformly moist with oil, but should not receive such a quantity as to be thrown out in any great volume at the ends of an ordinary pedestal, or axle-box, and wasted. But when proper means are adopted for preventing lateral waste, the pads may be partially immersed in the lubricant, or may obtain their supply of oil through wicks which dip into it.

Even when the old methods of siphon lubrication are adopted, pads are frequently used as auxiliary lubricating contrivances, since they remain moist for long intervals of time and keep the bearings [illegible] in the event of the siphon wicks, or [illegible] the lubricant.

[illegible] have been the advantages gained by the [illegible] that it is now almost universally used for [illegible] railway [illegible]. Not only is the friction kept [illegible] remarkably small, but the [illegible] has become almost a vanishing quantity. [illegible] bearings to be illustrated in this chapter [illegible] pads.

[illegible] the more fully saturated the pads are [illegible] and that the best result is obtained [illegible] of oil.

[illegible] —When the lower side of the [illegible] the surface is covered by a [illegible] against the [illegible] side of the brass. [illegible] is said to be "perfect." With [illegible] has [illegible] without difficulty, is [illegible]

[illegible] depends upon the completeness with [illegible] of the journal is kept wetted with [illegible] XV. page [illegible] taken from Mr. Tower's [illegible]

[illegible] proves that improved methods of lubrication [illegible] bearings but also [illegible]

[illegible] method of [illegible] friction [illegible] The [illegible] that the [illegible] in engine bearings [illegible] worth [illegible] of all kinds the [illegible] aimed at is [illegible] when even these [illegible] to the heavy load on the brass, [illegible]

[illegible] —Thus when, owing to the loads being [illegible] is low, a pressure film cannot [illegible] in the ordinary way, the best plan is to [illegible] by means of a pump actuated either by the [illegible] shaft [illegible] by hand. Of late years this method has [illegible] number of instances. Mr. Daniel Adamson [illegible] instance [illegible] heavy shaft which gave a pressure of 22[illegible] [illegible] kept running for years in this way without [illegible] whatever, the oil being pumped in by hand occasionally. This method of lubrication has also been found effective for pivot bearings. Without such aid, this form of bearing surface cannot be depended upon to carry loads exceeding 100 lbs. per square inch, and to carry even these loads it is necessary to make the surfaces of suitable material and to use substantial fatty oils. Thrust-block collar bearings might also be lubricated in this way with advantage.

Heating of Lubricating Films.—In the chapter on solid friction it was pointed out that the work done in keeping surfaces in relative motion is transformed into heat, and that the heat produced is exactly proportional to the work done. When the surfaces are separated by an oil film, the frictional resistance is wholly viscous, and the heat produced raises the temperature of the lubricant. This increase of temperature may be very considerable, for the film is very thin, a bad conductor of heat, and the motion of the lubricating fluid is direct. The heat produced goes, therefore, to increase the temperature of a very small volume of oil, from which, as the flow is not sinuous, the heat escapes but slowly by conduction. Professor Osborne Reynolds calculated that even when the heating of the journal is very small indeed, and the coefficient of friction low, the temperature of the oil film may be as much as 15° F. above that of the surrounding solid parts. In this way the fact that the friction of a journal is not proportional to the speed is explained, for the heat produced in the lubricating film decreases its viscosity.

The increase of friction with increasing speed is least marked when the lubricant is a mineral oil whose viscosity decreases rapidly with increase of temperature. Mr. W. D. Scott-Moncrieff states that in some experiments made by Mr. Napier and himself, it was found that the friction increased with an increase of velocity in the case of vegetable oils, but decreased with increasing speed with mineral oil.

When the lubrication is 'imperfect,' the loss of viscosity resulting from the heat liberated is not sufficiently great to compensate for the resulting thinner film and increased solid friction, and the frictional resistance is, therefore, greater.

The thermal units generated in a bearing per minute

$$= \frac{P\mu_1 v}{779}$$

P being the load on the bearing, μ_1 the coefficient of friction, and v the surface velocity.

The heat thus developed in the film has to be conducted through the shaft and bearing. But the quantity of heat liberated may be so great, and the lubricant, consequently, become so fluid, that it is incapable of sustaining the load, and the rubbing surfaces therefore close together and may seize.

Mr. Tower's experiments clearly bring out the fact, as also do those of Prof. Goodman, that the greater the viscosity of the lubricant, the greater the load a bearing will carry, providing the speed be not too high. The seizing, when the loads are considerable owing to the reduced viscosity brought about by increase of temperature, is somewhat more pronounced when mineral oils are used than it is with vegetable and animal lubricants, for, as previously stated, the viscosity of the latter oils does not fall off so rapidly with rise of temperature as is the case with the former. On this account mineral oils which have, at ordinary temperatures, much greater viscosity than fatty oils, can often be used without entailing increased friction.

Admissible Loads on Bearings.—The conditions which determine the area for a bearing necessary to secure cool running are very complex and render it difficult if not impossible, to give even an [illegible] whereby it may be calculated. Roughly, we may take it that friction always results either from actual abrasion or from the viscous or plastic resistance of the lubricant. When the speeds are low and the loads heavy, the more oily or greasy the lubricant, and the [illegible] the tendency of the surfaces in contact to gall and [illegible] then the smaller the necessary contact area becomes. The lubrication of a bearing is generally so imperfect with siphon lubrication that even up to speeds of 100 feet per minute the friction resistance is often many times greater than that obtained with

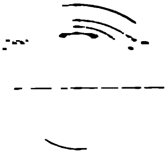

FIG. 91.

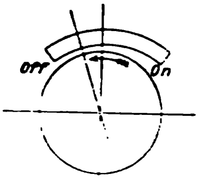

FIG. 92.

[illegible] At moderate or high speeds it is the viscosity of [illegible] keeps the surfaces apart, for wear makes the radius [illegible] larger than that of the shaft or journal, and [illegible] between them. The thickness of the film of [illegible] upon the form of bearing surface produced [illegible] according to the conditions of running and [illegible] lubricants.

[illegible] of load or viscosity the relative positions of [illegible] are also altered. With light loads, or viscous [illegible] the conditions obtaining, whilst with heavy [illegible] the relative positions of brass and journal are more [illegible] Increasing the load has the effect of bringing [illegible] together on the 'off' side, and causing them to [illegible] On this account, although experiment has shewn [illegible] limits the friction of a journal, and therefore the [illegible] is independent of the load, the local heating with great [illegible] greater than with small ones, although the total heat produced [illegible] in both cases, the sa[illegible] where the film is thin, excessive heating takes place, the rate of shear being great, and, more especially when mineral oils are used, the lubricant becomes less viscous, and, when the loads are too great, allows the surfaces to actually touch and abrade each other. It will be seen that increasing the viscosity of the lubricant beyond a certain point, although it may prevent actual abrasion, does not result in decreased friction, because although the tendency is to make the film more even in thickness and prevent the surfaces from touching, more heat is liberated by the increased fluid friction of the thicker oil.

The conditions, therefore, which determine the area necessary to be given to a bearing surface are, in some measure, those which arise from the heating of the film and the nature of the metals in contact. When working under normal conditions the thickness of the lubricating film should be so great that the friction and heating cannot injure either the lubricant or the metallic surfaces; but, as it is impossible with many forms of oil supply to guarantee a proper and perfectly regular rate of feed, and also wholly to prevent the access of grit, etc., the bearing must be made large enough to carry the load should the supply of oil be slightly insufficient.

However small the frictional resistance may be, the heat liberated must be allowed to escape from the journal and brass as quickly as possible, otherwise it will accumulate and so increase the temperature of the parts as to destroy the bearing. But, in practice, so many large masses of iron are necessarily in contact with the lubricating film, and they expose such a large surface to the air, that in the majority of cases the brasses and surfaces in contact with them, including the lubricating film, are not excessively heated, and the latter does not lose its load-carrying power to a serious extent. In the case of connecting rods and railway axle-boxes, the rapid movement through the air quickly dissipates the heat and enables comparatively heavy loads to be put upon them, even when the speeds are high.

Although most writers on lubrication are of opinion that the area it is necessary to give the opposing surfaces of a bearing depends, in great measure, upon the heating effect resulting from the friction of the rubbing surfaces, it is admitted that a satisfactory theory cannot be based upon this consideration alone, for the sustaining power of a bearing is often increased by using a more viscous lubricant, notwithstanding the increased friction and heating the change gives rise to.

If we assume that severe heating occurs only when, owing to a deficiency in the supply of lubricant, the coefficient of friction becomes independent of the load, the results obtained by some formulæ are in agreement, to some extent, with practice; but it is certain that many bearings would heat and seize long before the lubrication became anything like so imperfect as to bring this about. However, equations based on the assumption that the area of the rubbing surfaces through which the heat is dissipated should be [illegible] of the heat developed by friction give some results which [illegible]

[illegible] N, radius of journal [illegible] and coefficient of friction [illegible]

[illegible] (1)

[illegible] the journal or shaft, the area of the [illegible] the film = $4\pi r_0 h$ [illegible] 2) : one-half [illegible] that of the journal.

[illegible] are, however, seldom made to [illegible] ever more than one-fifth or [illegible] Making [illegible] the length of the brass in [illegible] within the area of the surface through [illegible]

[illegible] allowable to dissipate per unit [illegible]

[illegible] (3)

[illegible] (4)

[illegible]

[illegible] (5)

[illegible] varies inversely as N_0 [illegible] with [illegible] that the [illegible] and narrow. The small [illegible] is also partly to be [illegible] with their [illegible] wheels are better off in [illegible] speeds.

[illegible] the area that should be [illegible] we give in Table XCVI. [illegible] safe to use. The [illegible] varies in different [illegible] allowance be made for cases [illegible]

Fit of Bearings [illegible] *Brasses*.—Wherever possible, some [illegible] to the bearing by making it rather shorter [illegible] or spindle. The faces are then free to [illegible] in a direction at right angles to the circum[illegible] and uneven wear are thereby prevented. In [illegible] where an attempt has been made to prevent this [illegible] of the brass by making the journal smaller in the [illegible] at the ends, the device has had to be abandoned, circumferential grooves having been produced,and the proper formation of the oil pressure film prevented.

When the brass is semicircular, the whole of its surface should not be allowed to come in contact with the journal. The metal should be cut away somewhat at the sides, so that the bearing area subtends an arc of 45°, or less, on each side of the line along which the load acts. This enables the lubricant to get with greater ease to that portion of the surface which has to carry the load.

Light brasses are particularly to be avoided. Not only do they leave little margin for wear, but they are apt to distort or fracture through the crown just where the maximum load is carried, and where the oil pressure film forms. When such a fracture exists, the oil escapes through it, and the carrying power of the bearing is greatly reduced. The load also pinches in the sides somewhat and destroys, for a time at least, that difference between the radius of the brass and the journal upon which efficient lubrication depends.

TABLE XCVI.—ADMISSIBLE LOADS ON BEARINGS.

Description of Bearing.	Load in lbs. per sq. in.
Hard steel bearings on which the load is intermittent, such as the crank pins of shearing machines, . . .	3000
Bronze crosshead neck journals, ...	1200
Crank pins of large slow engines, ...	800-900
Crank pins of marine engines, ...	400-500
Main crank-shaft bearings, slow marine, ...	600
Main crank-shaft bearings, fast marine, ...	400
Railway coach journals, ...	300-400
Fly-wheel shaft journals, ...	150-200
Small engine crank pins, ...	150-200
Small slide blocks, marine engines, ...	100
Stationary engine slide block, ...	25-125
Stationary engine slide block usually, ...	30-60
Propellor thrust bearings, ...	50-70
Shafts in cast-iron steps, high speed, ...	15

The harder the surfaces in contact, the more accurate should the fit of the surfaces be made, for it is not until the faces are everywhere brought by wear to within a few thousandths of an inch of each other that good lubrication can be secured. White metals, on the other hand, are easily worked to a reasonable fit by hand, and soon wear to a perfect face.

In the case of shafts and spindles the fit should never be a tight one; sufficient clearance must be left for an oil film of sufficient thickness. Some engine makers leave a clearance of ·001 inch for each inch *diameter of shaft*, when the diameter is not less than 1 inch or greater than 6 inches. With this clearance, the bearings will not run hot when new, and soon wear to that condition which gives the best results.

To obviate the evil effects of strains resulting from the stresses machines have to bear, long bearings should be made so that they have freedom to move with the shaft as it deflects, otherwise the pressures are apt to become excessive at the ends.

Even when the workmanship is good, it is well to run the machine in the first instance at a moderate speed and load. This enables the bearing surfaces to bed themselves together properly and assume those curves which are the natural working ones.

Workmanship.—Owing to a want of accuracy in the fit of lathe spindles, and the spring of the centres when heavy, badly-balanced work is being turned up, it frequently happens that crank-shafts, etc., are turned out the bearing surfaces of which are not truly circular. Except in rare cases, this want of trueness is sure to cause hot bearings and give endless trouble. Indeed, however well a machine may be designed, if the parts be not accurately machined and properly put together, so that the contact surfaces shall slide or rotate accurately in their bearings, not only will there be undue friction and wear, but excessive strains will be thrown on portions of the machinery, and numerous failures from overheating will be the result.

To obtain anything like the efficiency and output which a machine, such as a steam engine, may be expected to give, good workmanship is absolutely essential, for want of accuracy of fit, and defective lining up, throw upon certain portions of the engine loads which the draughtsman never calculated they would have to bear, and the effects of which the engineman finds it impossible to counteract. This does not give the machine a chance of getting into that condition in which the friction is almost wholly due to the viscosity of the lubricant, and only slightly due to the actual contact of the metallic rubbing surfaces.

Wear of Bearings.—In the discussion of his report on friction experiments, Mr. Beauchamp Tower said * it seemed to him that the important practical inference is, that it is actually possible to so lubricate a bearing that not only would metallic friction be altogether done away with, and thereby the amount of power lost by friction be reduced, but metallic wear and tear would also be abolished. He would not say that such a result was actually possible in practice now, but it was a reasonable one to aim at in mechanism. By giving a profuse lubrication, and by having the brasses so arranged that there should be a uniform pressure all over their surface, it was possible to have wear and tear between metal and oil, instead of between metal and metal.

To a reduction in the frictional resistance of the machine we must therefore also add the increased life of its parts secured by the adoption of more perfect systems of lubrication, and both of these advantages may, if we use proper blends of oil, be secured without increased cost or waste.

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* Second Report on Friction Experiments. *Proc. Inst. Mech. Eng.*, 1885, p. 64.

Forms of Cylindrical Bearings.—*Bush Bearings.*—Light axles, spindles, etc., are usually supported by bearings which completely surround their rubbing surfaces. Such bearings are either plain bushes threaded over the spindle, or are composed of two portions which form an upper and a lower brass. As the weight is on the bottom brass the lubricant is supplied through an oil hole drilled in the top cap, and is spread over the bearing by a longitudinal groove. When the shaft is a moderately good fit, the results obtained by this simple form of bearing are excellent, for, as will be seen from fig. 93 (which is not drawn to scale), the annular space between the shaft and bush will, if the gap be not too large, be maintained full of oil by capillary forces, and the conditions of working will approach those of bath lubrication.

When the load is considerable, the oil-film becomes thin at the point of nearest approach on the 'off' side, the lubricant escapes at the ends, does not properly fill the gap between the upper brass and the journal, and the lubrication becomes imperfect. The increase of friction thus brought about may be seen when the upper brasses of the main spindle bearing of a foot lathe are removed. The friction will then be found to have increased greatly, for the oil fails to properly reach the 'on' side, and the bearing surfaces approach each other somewhat closely.

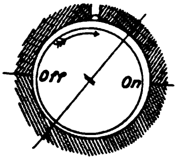

FIG. 93.

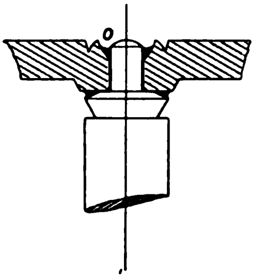

FIG. 94.

*Watch and Clock Bearings.** — As bearings of this kind have often to run for years without attention, they should be constructed so as to retain, by the action of capillary forces, a small amount of oil. The bearing of a watch or clock pivot is shewn in fig. 94. The oil sink O is deep and narrow, and holds a considerable charge of oil, which is prevented from spreading by the sharp angle formed by the edge of the surrounding groove. A portion of the shoulder is also bevelled to form a narrow recess in which oil can be stored. The back taper on the spindle below the collar, and also the boss on the plate, are to prevent, as much as possible, the oil from spreading.

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* *Friction, Lubrication and Lubricants, in Horology,* by W. T. Lewis, pp. 43-59.

Means for retaining a supply of oil are also provided when the pivots run in capped jewels. Such a bearing is shewn in fig. 95. Here the charge of oil is retained by capillary forces between the two jewels, which approach each other closely. One of these is perforated for the pivot, and the other is flattened to steady it laterally.

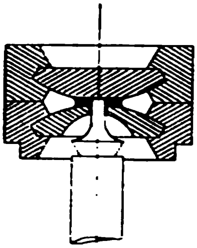


FIG. 95.

Pedestals.—The bearings or steps used for the support of shafts of any size are, as a rule, loose pieces of metal held in position by iron pedestals. When the load to be carried is very great, the pedestal is placed upon a sole-plate, which serves to distribute the load over a sufficiently large area of masonry. It also serves as a means of adjustment. In some cases, however, separate bearing pieces are dispensed with; the step then becomes a portion of the pedestal. When this is the case, to enable any wear to be taken up, and also to facilitate the removal and fixing of the shaft, the pedestal is fitted with a cap secured in position by bolts and projections. By reducing the thickness of the packing pieces which are placed between the cap and the pedestal, any slackness resulting from vertical wear can be taken up. Such a simple design is only suitable in cases where the speed and load are small. At one time the lubricant was nearly always supplied through a hole in the centre of the cap, and distributed along the surface of the shaft by two grooves which extended to within a short distance from the edges of the bearing.

The difference between the diameter of the shaft and that of its bearing being very small, the lubricant, even if a liquid one, remains between the surfaces in virtue of the play of surface forces. For line shafting and the main bearings of engines, upon which the load is often very considerable, the pedestals are always so designed that bearings or steps can be replaced with new ones when much worn.

Even now many very primitive designs are in use, which not only cause needless waste of oil, but also of power, for the friction coefficient is much larger than it should be. The shaft, in the cases alluded to, runs upon a bronze bearing, and to prevent the lubricant running off at the sides, and being wasted, the latter is only supplied in small quantities. The proper lubricating pad or film is consequently unable to form, and the faces are always, to some extent, abrading each other. On this account, pure mineral oils deficient in greasiness give but poor results when used for such bearings.

An improved pedestal, shewn in the accompanying fig. 96, is now being very extensively used. Only a short arc of the cap and brass are in contact, or nearly so, with the shaft, the spaces at the sides being occupied by felt pads kept moistened with oil from a siphon lubricator. With this arrangement, the frictional losses are comparatively small. Better bearings even than these are now being brought into use. They are so contrived that the lubricant is thrown over the shaft in a continuous stream, forms a thick lubricating film, and is again returned to the bearing after passing into a reservoir below. Under these conditions the lubrication is perfect, *i.e.*, viscosity has free play, and mineral oils, with a slight admixture of fatty oils, answer admirably, if the surfaces be of the proper materials.

In such bearings, the lubricant is in continuous circulation, the same charge often lasting for nearly twelve months.

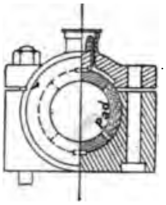


FIG. 96.

Fig. 97 shews such a bearing, made by the Brush Engineering Co., Limited, Loughborough. Here the pedestal forms an oil reservoir from which the lubricant is raised by means of an endless chain slung upon the shaft, by which it is kept in motion. The lower part of the chain dips into the oil-bath and carries up with it a thick film of oil, which is distributed over the top of the shaft through the longitudinal oil-ways. To prevent the oil being thrown about, and thus wasted when it is expressed at the sides of the bearing, splashers are cast at the ends of the pedestals, to collect and return the oil to the reservoir.

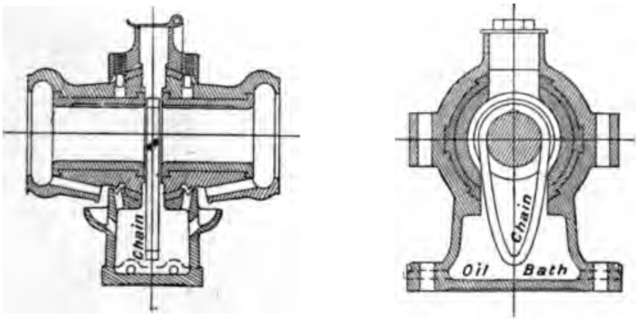
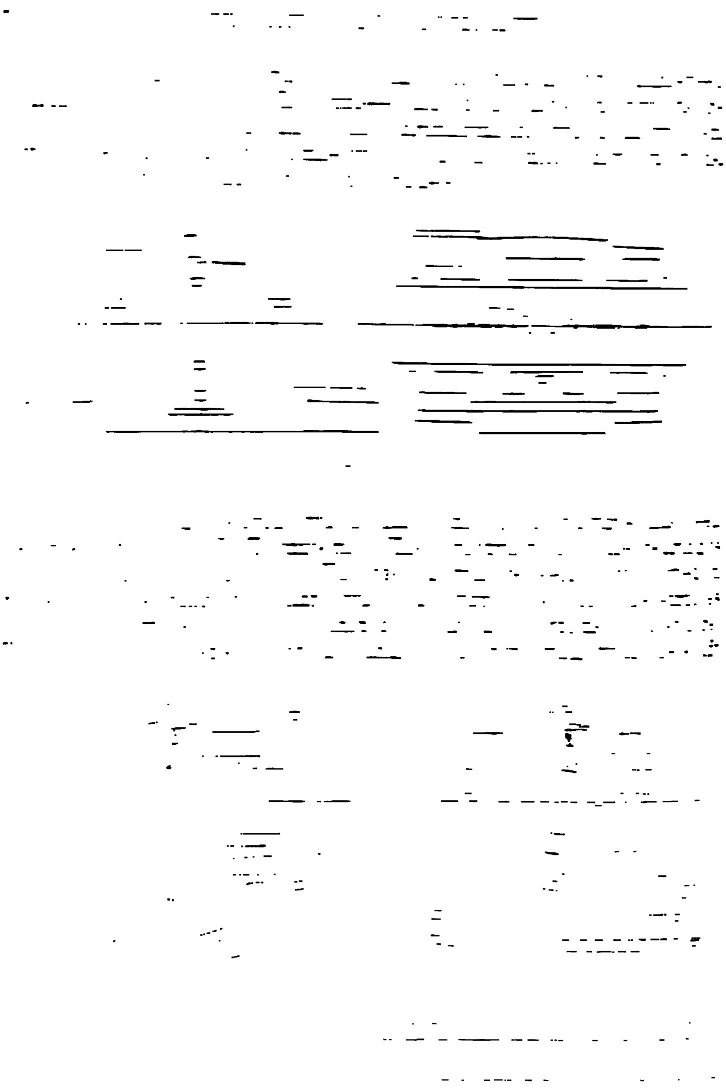


FIG. 97.

Some care is necessary in selecting the material of which to make the oil lifting chains, for the lubricant is apt to become somewhat acid with age. Iron, steel, or brass, used alone, work well, but on no account should two varieties of brass or steel be used together, one for the pins and another for the links, as they set up electro-chemical action, which destroys them.



[illegible]

and dripping [illegible] scraped off [illegible] flows thence [illegible] to the journal.

In the bearing made by Thomas Parker, Limited, Wolverhampton, is shown in fig. 95 the oil is lifted from the reservoir by means of a loose ring threaded on to the shaft. In other cases a loose collar takes the place of the chain or ring, whilst some makers of bearings place a felt pad along the top of the upper brass, to act as a strainer for the oil. The pedestal casting in such cases forms a splasher projecting beyond the bearing, and serves to collect the oil thrown out at the ends and return it to the reservoir.

When the shaft is heavy, it is well to make the lower brass rest in a cylindrical seating concentric with the shaft, and to prevent it from rotating by suitably shaping the bearing surfaces of the brass in the cap. This enables the lower brass to be removed by merely turning it round when the shaft has been lifted only a fraction of an inch.

In some instances, the direction in which the load acts is not by any means a vertical one, owing to the strain of a belt or some other lateral force. The dividing line between the brasses should then be at right angles to the direction of the resultant pressure on the journal, and, therefore, not horizontal.

The practice of making the brasses in three or more pieces is sometimes resorted to, as it enables the wear to be taken up without removing the bearing pieces. In many cases, however, the division between the separate pieces allows the lubricant to escape just where the maximum pressure of the supporting film should be, while in all such cases the sustaining power is reduced and the friction coefficient increased. When there is only one brass the shaft can move into that position which has been shewn to give the lowest coefficient of friction; but when the bearing consists of two or more separate pieces of metal, each bearing piece must be free to move somewhat and adjust itself so as to occupy its proper position with regard to the shaft, and each 'on' edge must be properly lubricated. When such adjustments cannot freely take place and the load is considerable, the bearings give a high coefficient of friction and easily run hot.

For high speeds it has been found advisable to make the bearings of large area, and cast-iron is then often used, for the loads per square inch in such cases are small. The longer the bearings are, the more necessary does it become to construct them as shewn in figs. 97 and 98, so that no undue strain shall be thrown upon their ends if the shafting should be somewhat out of line or be bent.

Many high-speed bearings are now not only fitted with two rings or chains slung on the axle and rotating with it so as to pick up the oil, but they have also small oil pumps, driven by a cam on the axle, which deliver the oil on to the bearing in a constant stream. Such extreme precautions against the possibility of a failure in the proper supply of the lubricant are by no means unwarranted, for they insure a low coefficient of friction, and almost wholly prevent wear of the bearing surfaces.

Axle-boxes.—In the case of the bearings of railway vehicles, the brass or step rests upon the journal, and the load acts vertically downwards. The journal usually projects beyond the wheel, and can be inclosed in a dust-proof box fitted with a door at the front to enable the condition of the journal to be ascertained at any time. But on some locomotive engine bearings the axle-box is placed inside the wheels, and cannot be designed on quite the same lines as railway coach bearings.

Locomotive driving and trailing bearings are of brass lined with white-metal, the lubricant being supplied by syphons fixed above them. In some instances an oil reservoir is placed in the axle-box keep, and a lubricating pad fixed therein, [illegible] pad presses against the under side of the axle.

The method of cutting oil-ways along the centre of the bearing and making it a good fit at the sides, which in the case of driving wheel bearings, is considered to be the best practice, is not always followed in the case of other locomotive engine bearings, for the driving axle has to carry the thrust of the piston as well as the vertical load. The groove, by, to some extent, preventing the pressure film from forming, causes the crown of the bearing to wear more rapidly than it otherwise would do, and tends to prevent the side thrust of the connecting rod from developing side play. The trailing wheel bearing, on the other hand, is cut away at the sides, the arc of contact being about 90°, so as to give the oil free access from the pad to the crown of the bearing. The single groove along the crown is also sometimes replaced by oil-ways which inclose the area over which the pressure film should form. Locomotive engine axle-boxes which are placed inside the wheels, and are not fitted with a door to enable the pad to be easily got at and cleaned, have auxiliary syphon lubricating appliances. Provision must be made in many cases to take the thrust due to the brake blocks by making the arc of contact of bearing and axle of sufficient width. Locomotive bearings lined with good white metal, and having an oil-way across the centre of the brass, will carry 250 lbs. per square inch, the width of the step being calculated on an arc of about 90°.

The most satisfactory tender and bogie axle-boxes are constructed upon the lines of those used for the coaching stock, drawings of some of which will now be given.

For railway vehicles which have brake blocks on both sides of the wheel, and are, therefore, only subject to slight lateral pressure, the best practice is to make the arc of contact short, the brass long in a direction parallel with the shaft, and to supply the lubricant by means of a pad pressed against the underside of the journal.

An axle-box of this kind is shown in fig. 100. Here, the lower portion of the box forms a reservoir for the oil, into which thick cotton wicks hang from the pad. The oil rises in the capillary pores and keeps the pad and journal well moistened. The brass is a loose piece which, by lifting the box a short distance from the axle, can be taken out and examined when the door at the front is open. No oil grooves or holes of any kind are cut in the face of this brass, as they would more or less prevent the pressure-film from forming properly. To prevent the oil from escaping from the box, and to keep out dust and dirt, the door is made a good fit, whilst on the inside the axle is grasped by wooden shutters sliding in grooves. All the oil expressed at the inside edge of the brass passes into the small auxiliary reservoir, and is picked up by the disc fixed to the axle and transferred to the bearing by a wiper.

Owing to the fact that these boxes are kept cool by being brought into contact with the open air, and that there is a good deal of vibration and variation in the direction and intensity of the pressure between the surfaces, the bearings can be made to carry heavier loads than can stationary bearings of similar design, running at equally high speeds.

In this country it is the custom to make the steps of bronze, and to lubricate with mixed oils. It would seem, however, that when the bronze is replaced by a suitable white-metal, pure mineral oils can be used and a great saving effected in the cost of the lubricant. The customary load put upon bearings of high-speed vehicles is about 250 lbs. per square inch.

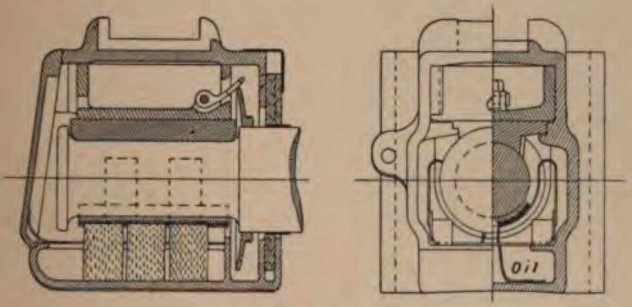


FIG. 100.

Grease Boxes.—A fluid lubricant is only, as a rule, used for the axle-boxes of quickly-moving vehicles; for wagons, grease is often preferred, the frictional resistance at starting being smaller with plastic lubricants than with fluid ones.

A grease box, Ellis' patent, such as is used on mineral wagons, is shewn in fig. 101. In some respects it resembles the box used for oil, but differs from it in the important particular that the lubricant is supplied through large holes near the ends of the bearing, the melting-point of the grease being such that if the bearing becomes a little warm the grease becomes fluid, and finds its way upon the journal.

Spindle Bearings.—The Hon. C. A. Parsons, F.R.S., has lately introduced a very ingenious bearing for shafts running at such extremely high speeds as 9000 revolutions per minute. It is impossible to balance such quick-running shafts so accurately that the centre of [illegible] shall coincide with the centre line of the journal. To prevent undue pressure being put upon the bearing, and also the vibration which would result from making the shaft a somewhat loose fit, the [illegible] threads upon the shaft—one upon the other—several sleeves, the outside one of which fits the pedestal casting. Between each bush oil-films form which, by their viscosity, damp all vibrations. All the bushes need not be free to rotate. These bearings are used for the shaft of Parson's turbo-motor, the oil being supplied continuously to the bearing by means of a pump, which keeps up a constant circulation of oil.

The bearing surfaces of moderately high-speed spindles are nearly always coned, so that any wear can be taken up by moving the pedestal or spindle laterally, and the surfaces upon which the spindles run are often made of white-metal. The best spindles are obtained by shaping them from hard rolled bars of steel, the metal, in this state, being flexible and of very even texture.

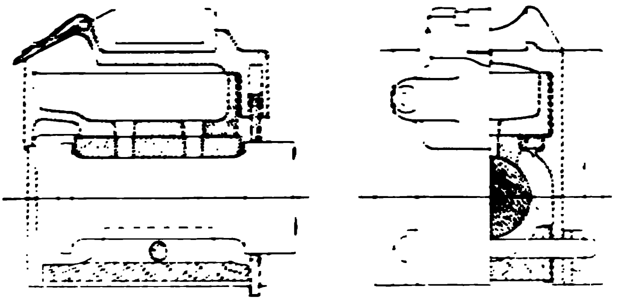


FIG. 101.

The footsteps carrying the spindles of spinning mules, twiners, etc., are sometimes made of solid brass, with a cup-shaped reservoir for oil. The spindle runs in a hole in the centre of this reservoir, and is, therefore, always perfectly lubricated. Upon the cup-shaped reservoirs rests a frame, carrying small covers which effectually retain the lubricant and prevent it from running down the frame or spindle board and from being thrown about.

Loose Pulleys.—Loose pulleys as a rule are merely bushed with bronze, and run upon accurately turned shafts, their lateral motion being prevented by the fixed pulley on one side and a collar on the other. Sometimes such pulleys are only supplied with a drop of oil occasionally, in other instances they have screwed into them a small oil-cup which feeds very slowly.

Smith's self-oiling pulley, which has lately been introduced, is shewn in fig. 102. The boss of the pulley is made of sufficient diameter to give room for a large bush, which is chambered externally, so that, when in position, it provides a large annular space for oil. The chamber is interrupted by three perforated ribs, which serve to carry the oil round when the pulley is in motion, and to stiffen the bush. From this chamber the oil, as it is carried up, passes to the bearing through a number of radial holes in the bush, being prevented from escaping at the ends by two circular grooves having oil-ways connecting them with the oil-chamber. The portion of the shaft upon which the pulley runs is thus regularly and automatically lubricated, and when supplied with a non-gumming, fairly neutral lubricant, only needs occasional attention.

Variable-Load Bearings.—Crank pins, cross-head pins, and all

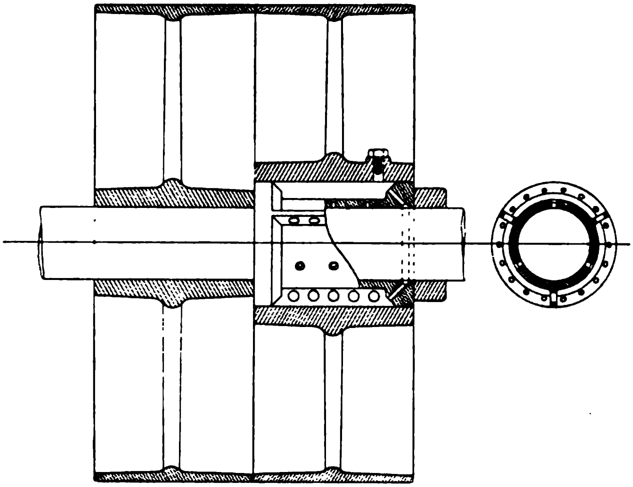


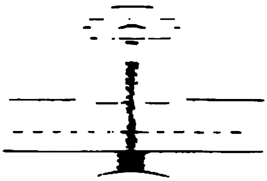
FIG. 102.

bearings upon which the direction of the load is quickly reversed and the bearing surfaces thereby periodically parted, will carry extremely heavy loads. In such cases the lubricant is drawn in between the surfaces as they part, while the load remains on the bearing for so short a time that the oil-film is only partially pressed out. But these conditions do not at all times prevail, especially in locomotive engines, which have to start away with a heavy load behind them. The bearing upon which the iron or steel crank-pin is pressed has consequently, in such cases, to be made of very hard white-metal, which will not squeeze out under the great pressure put upon it.

It must not be assumed, however, that the pressure on the crank pin is measured by that of the steam on the piston, for, at ordinary running speeds, the inertia of the moving parts tends to equalize the pressures on the pin very considerably.

The load on a cross-head pin may be made much greater than that

[illegible]



[illegible]

[illegible] moistened.

The eccentrics [illegible] of steam engines work under much the same conditions [illegible] the crank pins. Owing, however, to their large diameter, [illegible] velocity of rubbing is greater, and they will not carry such heavy [illegible]

The reciprocating motion of an eccentric is generally so small, even when running, that ordinary siphon oil-cups are easily filled by hand. When, however, the speeds are great, the oil is led through pipes leading from siphon lubricators to wipers. The eccentric straps of locomotives are usually made of steel or iron lined with white-metal which works upon cast-iron sheaves.

Pins with Reciprocating Motion.—In many cases, pins have to carry a steady load, and the surfaces only move relatively to each other through a small angle. In some instances, the load that can with safety be put upon the bearing is only small; a greasy lubricant must therefore be used and the surfaces hardened. The slow reciprocating motion of the surfaces, and the constant pressure upon them, tends to expel the oil from the faces rather than to draw it between them. Such bearings are by far the most difficult to lubricate and keep in order, especially if every care has not been taken to make them of such metals as will work well together. If the oil be supplied by one groove running along the side opposite to that which carries the pressure, there is very little chance of its being able to spread itself over the rubbing surfaces. Two parallel grooves, one on each side of the centre line of the load, not very far apart, and arranged so that all parts of the surface shall be exposed to the oil resting in them during some portion of the motion, serve their purpose most satisfactorily.

Plane Surface Bearings.—*Loading of Plane Surface Bearings.*—In the case of plane surfaces the conditions which determine the frictional resistances are by no means so uniform as those which determine the friction of cylindrical bearings. Indeed, the relative positions of the moving surfaces, even in the case of pivots and collars, vary with the direction in which the load acts, and the sustaining power of the film is thereby greatly affected. But, even when the conditions are most favourable, the load they will carry, except at low speeds, is only 60 or 70 lbs. per square inch, and even with such loads the rate of wear depends largely upon the nature of the rubbing surfaces and the quality of the lubricant. The principal forms of bearings of this description are slide-blocks, collars, and pivots.

Slide-Blocks.—When it is necessary to so constrain a moving piece, or any part of it, that the motion shall be one of translation only, straight guiding surfaces termed slides and slide-blocks are generally used. Parallel link-motions, although they give a much smaller coefficient of friction when new, are more complicated, and the effects of wear are not so easily allowed for.

The loads at which oil pressure-films can form on plane surfaces being only moderate ones, slide-blocks are generally of cast-iron working upon cast-iron or steel. The slide-blocks are, however, sometimes lined with gun-metal or white-metal when the speeds are great. In America, chilled cast-iron surfaces have been introduced. The chilling is effected in diagonal strips separated by equally broad spaces of soft metal. This gives the surfaces that degree of unevenness which enables the oil to be trapped and so keep the surfaces apart. Oil-ways may be cut in long slide-blocks so as to distribute the oil over the surfaces and enable it to reach the edges, but as the [illegible] quite reach the edges, the oil cannot [illegible]

[illegible] slide-blocks range from 20 to 120 lbs. per [illegible] the speed and the nature of the rubbing [illegible] works well upon cast-iron [illegible] per square inch is reached, gun-metal or white [illegible] When the load is light and the [illegible] is very small indeed, especially if the slide [illegible] in the latter case.

[illegible] but when the crank is not [illegible] that their surfaces are [illegible] The oil so placed then [illegible] with every change of angle of the crank shaft. [illegible] by siphon cups or other [illegible] the ends of the bars, where the [illegible]

[illegible] Messrs. Musgrave & Sons have [illegible] which is [illegible] in an [illegible] and the [illegible] is [illegible] by the pin upon [illegible]

[illegible]—Collar-bearings, unlike slide-blocks, which only [illegible] moving parts, and only have to bear intermittent [illegible] carry the thrust resulting from the weight [illegible] by the pressure of the water on the [illegible] small. With [illegible] that the [illegible]

[illegible] were made with very [illegible] Under such conditions it appears that 70 [illegible] per square inch is the utmost that can be put upon [illegible] and when the speed is [illegible] even smaller loads [illegible]

[illegible] carry the loads in drilling machines, lathes, etc. [illegible] heavy loads put upon them, that to prevent seizing, the [illegible] of the hardest steel, have numerous oil-ways cut in them, and [illegible] with good fatty oils. Small bearings [illegible] as the spindles of drilling machines, where the [illegible] have steel faces which often work under loads [illegible] 300 lbs. per square inch, and in exceptional cases as [illegible] per square inch has been put on a collar for a short time.

[illegible] the proper lubrication of the faces of the thrust blocks [illegible] which screw shaft collars work, the thrust block [illegible] in such a manner that the collars are exposed in places and dip [illegible] oil bath, or press against an oiled pad. In this way fairly perfect lubrication is secured, provided the load per square inch be not greater than 70 lbs. per square inch. However, as the efficiency of a thrust block at the best is not high, the heat liberated is great, and the block must, when the bearing is a large one, be kept cool by a water jacket.

Pivot-Bearings.—When the thrust to be carried acts upon a vertical shaft, instead of carrying the load on collars the end of the shaft may rest upon a circular face or pivot-bearing. This form of bearing permits of bath lubrication, for the footstep may be so designed that it forms a vessel which can be kept full of oil.

Fig. 105 shews a bearing surface such as Mr. Tower used. The oil is admitted through the centre hole and passes into two radial grooves. From these grooves the lubricant is carried between the surfaces, and is expelled by the pressure upon the pivot. The track of the oil varies at different parts of the surface, a portion being expelled at the edges. This sets up a continuous circulation of the oil from the centre of the bearing to the margin of the footstep, and up between the cylindrical portion of the bearing and surrounding bush.

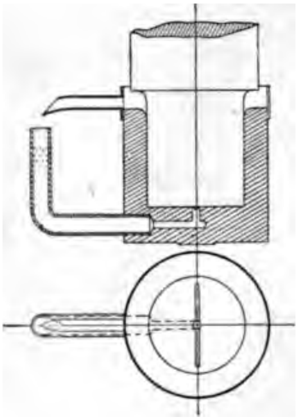


FIG. 105.

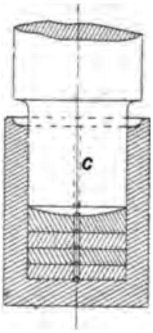


FIG. 106.

The only reliable experiments on the friction and sustaining power of pivot-bearings are those made by Mr. Tower with this pivot. In these experiments are given the greatest loads which he found a pivot-bearing would carry without actual abrasion of the surfaces taking place. For the actual results, see p. 70.

Figure 106 represents a footstep-bearing somewhat similar to one designed by Mr. Ford Smith. Here the circulation is as shewn by Mr. Tower, but the actual bearing consists of four discs of hardened steel all perfectly free to revolve with the pivot. Through the centre of all four washers is drilled an oil hole, and radial grooves are cut in the faces. The passages C enable the oil to circulate between the washers and up the side of the shaft. By using four washers, five friction surfaces are formed, and the films are increased in number to the same extent.

This enables the temperature of the films to be kept more nearly that of the masses of metal, and should one become a little overheated and tend to seize, the other faces move relatively faster and allow it to cool again. As a means of relieving any local pressure which might result from the springing of the shaft, it has been suggested that one of the loose washers should be made convex on one face, as shewn, so as to fit in a concave face on the opposing washer or pivot.

When the pressures exceed 160 lbs. per square inch, the surfaces must be made of hardened steel working upon a similar face, or upon dense cast-iron or bronze. Should the load exceed 300 or 400 lbs., a force pump must be resorted to, and a continuous stream of the lubricant forced between the pivot and footstep. As much as 1 ton per square inch can be supported by this means without any difficulty.

Piston Rod Packings.—The conditions under which the bearing surfaces of piston-rods work, although the surfaces are of cylindrical form, are very different to those of journals or shafts, for the motion is a longitudinal one instead of a rotary one. It is seldom that they are used as guides, the load on them being restricted to that resulting from the devices used to take up the wear and keep the joints steam-tight. It is the slide-blocks and piston head which should be made to act as guides, and if these be not accurately fixed in line or become a little loose by wear, the packing will blow unless it is made free to move laterally with the rod.

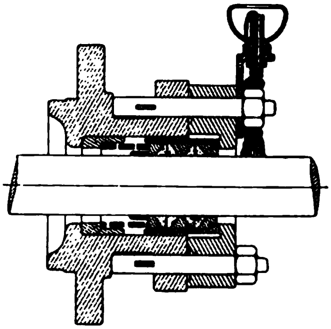


FIG. 107.

In fig. 107 is shewn a form of metallic packing, known as the "United Kingdom Metallic Packing," which has given good results on locomotives. Split rings of white-metal, of triangular section, are held in a brass frame, which is free to slide laterally against a surface upon which it is pressed by the steam and a strong spring. As the white-metal wears away it is kept in contact with the rod by the pressure of the spring. For such packings to work satisfactorily the rod must be quite true, and free from shoulders at the ends. Good lubrication is also absolutely necessary. It is generally supplied by means of a small siphon or drop lubricator to a pad resting upon, or even surrounding, the piston rod, which is thus kept moist with oil.

Rolling Contact Bearings.—*Ball-Bearings.*—Although under the conditions of running which obtain in practice at ordinary speeds and with heavy loads well lubricated bearings of the usual character give, perhaps, the smallest coefficients of friction available by any means at our disposal, when the loads are light and the speeds low better results can be obtained with ball- or roller-bearings. They are consequently coming largely into use for cycles, light vehicles, various kinds of clockwork, etc.

The coefficient of friction is not affected by changes either in the load or the speed, and only to a very slight extent by the viscosity of the lubricant, which only tends to replace solid friction by viscous friction, and thus reduce wear.

The ball-bearings for cycles are being made as dust-proof as possible, and are also frequently provided with an oil-bath. This enables the bearing surfaces and balls to be kept clean and well supplied with the lubricant. The balls run on coned surfaces, so designed that any wear can be taken up by lateral adjustment and an accurate fit secured.

In all cases where ball-bearings are used, it is absolutely imperative that there should be freedom from shock or jar, for a smart blow will either break the balls or destroy the accuracy of the surfaces upon which they run. Although the crushing weight of a ball $\frac{1}{4}$-inch in diameter is as high as 5000 lbs., the load it will carry without breaking is only about 200 lbs. The crushing load is proportional to the square of the diameter. The ball paths of bicycles are frequently made concave, their radii being somewhat larger than that of the balls. Each ball has then two points of contact. When the distance between the races is carefully adjusted, and the balls are accurately centred between the faces, the frictional resistance is that due to rolling only, and the pressure on the balls is merely that due to the load. If, however, the balls should work slightly out of position, they jam, and the load upon them, and therefore the friction, increases. The best design of ball-bearing is shewn in fig. 108. Here, each ball runs upon three races instead of two. The friction, however, is not increased on this account, as the resistance to rolling friction is proportional to the load, and therefore independent of the number of points of contact, always provided that at each point of contact the friction is rolling friction only. True rolling friction is obtained by making the angle of the cone forming the inner path such that its apex falls on the centre of the axle at the same point, A, as does a line drawn through the two points of contact on the outer cup. In this design, the balls cannot become displaced, the friction wholly results from simple rolling, and the balls firmly control the hub laterally. It is necessary to make the clearance at the point C, between the cone and cup, very small, so as to exclude dust. Now it will be noticed that if the cone be not properly adjusted, and the

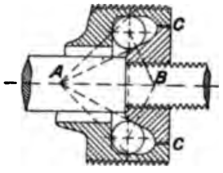


FIG. 108.

balls run loose, the faces at C may come in contact and the friction be greatly increased. On this account it is essential that the cones be very carefully adjusted, so that the balls shall not jam on the one hand or run too loose on the other.

Fig. 109 shews a hub complete, fitted with balls, each having three points of contact.

Roller-Bearings.—In cases where the load is steady, but too great to allow of the use of balls, rollers are now frequently used. The great advantage they—for some purposes—possess over plain bearings arises from the small resistance to motion they offer at very low speeds. This is a very important consideration where heavy structures, such as swing bridges, have to be moved, or when vehicles have to be started and stopped frequently. 'Great Paul,' the big bell at St. Paul's Cathedral, which, with its headstock and other moving parts, weighs nearly 25 tons, is now supported on roller-bearings. The friction is one-seventh less than was given by ordinary bearings. Roller-bearings have been in use for many years in cases where the structure was only occasionally moved, but it is only lately that they have been introduced for vehicular purposes, although even now they can only be said to be in their experimental stage. We shall illustrate several designs made by the Roller Bearings Co., Limited, of London. Fig. 110 is the form supplied for motor-car wheel bearings. The seven rollers are held in position by a floating cage, which keeps them in line with the journal upon which they run. To prevent end-play balls are used.

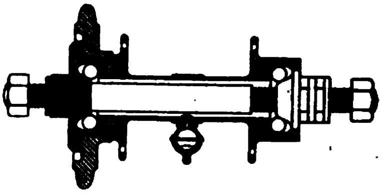


FIG. 109.

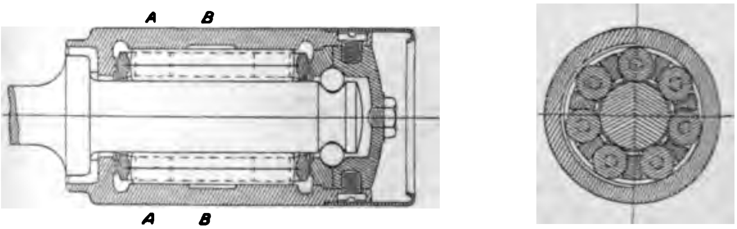


FIG. 110.

For tram-cars the bearing shewn in fig. 111 has been designed. Here the rollers are carried in a cage as before, but undue end-play is prevented by a kind of pivot bearing.

Bearings of this description require very little lubrication; indeed, only just as much oil as will prevent rusting is required.

Methods of Applying Lubricants.—*Efficient Lubrication.*—It will be seen that it is possible to take advantage of the low frictional resistances which perfect lubrication gives without either incurring waste of oil or undue complication of parts. At the present time, the scientific design of bearings can perhaps only be regarded as in its infancy. But it is inevitable that, as the true principles of lubrication come to be better understood, the use of solid or semi-solid lubricants will be largely given up, and for all quick moving machinery the oil-bath or its equivalent will be almost universally used.

Pump Circulation.—Instead of placing a reservoir beneath or above each bearing, and allowing the latter to automatically lubricate itself, the plan is often adopted of supplying the bearings of engines, dynamos, etc., in an engine-house, from one or more raised tanks into which the oil is pumped from a common well, to which the lubricant gravitates as it runs off the brasses. By this means the oil is used over and over again, and can be strained, clarified, and replaced as desired. This method involves the use of a rather intricate set of supply and return pipes, and the bearings must be designed so that the waste oil may be collected without loss as it runs off the steps, slides, etc.

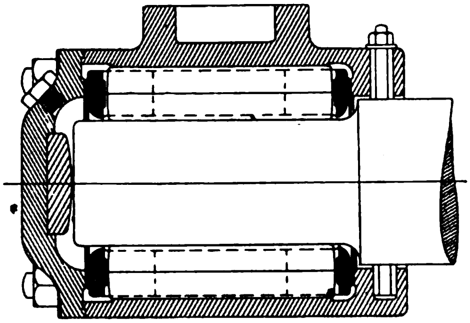


FIG. 111.

Siphon and Drop-feed Lubrication.—Although the old forms of lubricators are being dispensed with to a large extent in favour of more perfect automatic contrivances securing more or less perfectly the advantages of bath lubrication, it is unlikely that they will be displaced entirely, for there are cases in which the conditions of working are such that the lubricant cannot be recovered, and must be supplied continuously in small quantities. Slide bars and piston rods are cases in point. Siphon and drop-feed lubricators are largely used for these and other purposes.

The siphon lubricator used for lubricating a piston rod, shewn in fig. 107, may be referred to. It consists of a shallow reservoir in which the oil is stored, and a central tube, leading to the part to be oiled, and having its upper orifice raised a little above the oil surface. Through this tube is passed a wick of cotton or worsted, one end of which is immersed in the oil and the other end hangs downwards. The capillary space between the fibres of the cotton or worsted [illegible] up and passing down the tube, converts the [illegible] into a number of small syphons, which slowly drain the oil [illegible] and thus lubricate the opposing surfaces below. The theory of this action is fully described in the chapter on Superficial Tension [illegible].

The [illegible] lubricator, Fig. 112, made by Messrs. Mather & Platt,* consists of a small vessel [illegible] having a passage leading from the bottom, [illegible] in which is a small valve which can be regulated as desired. The discharge tube terminates in a nozzle [illegible] glass tube, which enables the engineman to see the rate of feed. Such lubricators, however, are liable to be

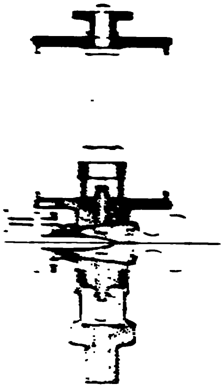


FIG. 112.

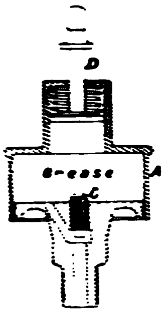


FIG. 113.

[illegible] especially if the valve and outlet [illegible] and the oil be not strained.

[illegible]—When it is considered desirable to use grease as a lubricant the Stauffer "tell-tale" lubricator can be recommended. This is shown in fig. 113 The rate of feed is regulated by the screw C; the small piston D, being forced down by the spring, indicates when it is desirable to screw down the cylinder A.

Steam *Cylinder Lubricators.*—Grease cups are now seldom, if ever, used for lubricating steam cylinders, for they are not capable of feeding suitable oils with the necessary regularity, and it is now recognized that grease should not be used in cylinders. A cup designed like a grease cup may, however, be used as a ready means of introducing a charge of lubricating oil into a steam space against the steam pressure, and there are instances when it is advisable for this to be done. The usual design of such a lubricator is shewn in fig. 114. By opening the upper tap whilst the lower one is closed, the centre globe may be filled with oil. On shutting the upper tap, and more or less opening the lower one, the lubricant is allowed to flow into the steam space below, whilst the steam flows into the globe.

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* A. Howat, Eng. Patent No. 20,205. (1893.)

It has been found more convenient and more economical to replace this simple method by an automatic contrivance which will feed the lubricant slowly, as it is required. One of the earliest and most satisfactory instruments of this class for locomotive engines is the Roscoe * lubricator shewn in fig. 115. The delivery pipe, which passes well in to the steam pipe, must be of such diameter that both the oil from the lubricator, and the water resulting from condensation, can flow away freely along the bottom, and allow live steam to enter along the upper part of the bore.

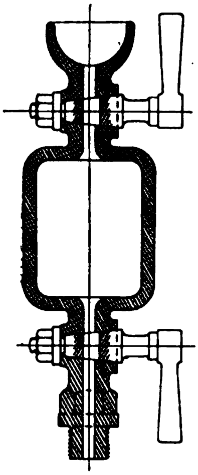
FIG. 114.

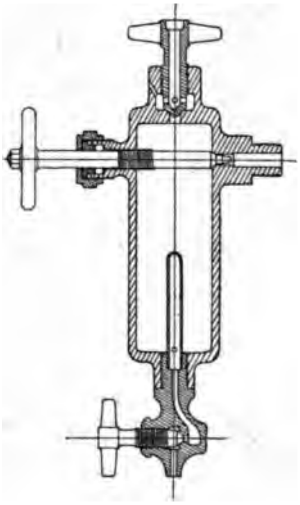
FIG. 115.

In many of these forms of lubricator designed for cylinder work the oil is displaced from the lubricator by the weight of a column of water produced by the condensation of steam from the boiler or steam pipe. Should there, in this form of lubricator, be a deficiency of water resulting from a check in the rate of condensation, the lubricator may cease to feed. When the boiler is supplied by means of an injector, air, as well as water, is thrown into the boiler. Air thus introduced remains in the pipes leading to the lubricator, or even in the upper parts of the lubricator condenser, and by remaining there and pre-

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* James Roscoe, Leicester, Eng. Patent No. 1337. (1862.)

venting steam from entering, checks condensation and stops the feed of oil.

A pipe too small in diameter, or not having a regular slope towards the steam pipe, will become choked with the liquid and prevent the lubricator working.

The Roscoe lubricator consists of a chamber which can be filled with oil from above. Near the top of this chamber is the delivery passage, which can be opened or closed to any desired extent by means of a valve. There is also in the centre a vertical tube, the upper end of which is closed, and the lower end perforated to admit water or oil. Upon the vessel being filled with oil, the tube remains full of air until the delivery valve is opened, when, the steam entering the lubricator, the air is compressed. The steam then rapidly condenses, and the water falls to the bottom. So long as the engine is running, the delivery valve is left slightly open, with the result that steam or water slowly enters the lubricator, and the oil slowly finds its way out. Should steam be shut off, the pressure in the lubricator is relieved, the air expands in the central tube, and a quantity of oil is driven out which serves to keep the parts lubricated until steam is again turned on. The amount of opening which must be given by the driver to the delivery valve when the lubricator is fixed on a locomotive depends upon the number of stops which have to be made by the train, the temperature of the air, and the extent to which the steam is throttled by the engine regulator. An experienced driver can judge these points very satisfactorily, and obtain good results without waste of oil.

For steam cylinders, during the last few years, sight-feed lubricators have been very largely used. Of these lubricators, and there are numerous designs upon the market, only a few can be relied upon to feed regularly under all conditions.

A lubricator which meets these conditions fairly well is that designed by Mr Ottewell.*

The valve A (fig. 116) can be opened so as to allow steam to enter from a current which passes from the boiler to the steam pipe through a T piece screwed to the nipple H. The steam, condensing in G, fills the whole of the lubricator with water, except the lower chamber R, which contains the lubricant. The valve A, being left slightly open, allows the water in G to flow slowly into the steam pipe, and steam to enter the chamber to make good the deficiency, in the same way as the valve does in Roscoe's lubricator. When it is desired to feed oil, the valve C is opened. Oil drops, rising through the glass tube, enter the chamber G, and, with the escaping water, pass by the plug valve A. As the oil passes away, water descends through T and rises in R.

This lubricator has been found to work well on locomotive engines. For stationary engine work, however, it has been found advisable to make some slight alterations.

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* A. D. Ottewell, Eng. Patent No. 21,257. (1895.)

The lubricator may be considered as a 'Roscoe' cut into two parts and furnished with a sight-feed device, which makes it more easy to regulate.

Another design* which will feed regularly is shewn in section in fig. 117. The branch S is coupled up to the boiler, and the branch H to the steam-pipe a short distance from the point where it joins the cylinder steam chest. Through these pipes there is a constant flow of steam, which can, however, be stopped by closing a cock on the boiler.

To fill the lubricator, the valve D is placed in the position shewn, and steam is turned on for a time. When the lubricator has cooled somewhat, and the reservoirs E and F and the glass tube G are full of water, D is closed by means of a handle. Before attempting to fill with oil, the fitting must be allowed to cool (these precautions need only be taken when the lubricator is new and quite empty). A is then unscrewed, and all the water that will pass away allowed to do so by opening W. Closing W, the chamber F may then be charged with oil. Steam having been allowed to pass through S and H, the centre of the plug D is filled with steam at the pressure of the boiler. Here it condenses, and when the upper port is open, the water enters E, passes down the port near the glass sight-tube, and then up the gauge glass itself. This current of hot water serves to keep the lubricator warm—a very necessary feature when very viscous mineral oils are used—and also to keep the glass full of clean water. The oil can be supplied at any desired rate by opening C. It is caused to flow mainly by the difference in the head of the two ports in the side of the plug D, and as it escapes from the nozzle into the

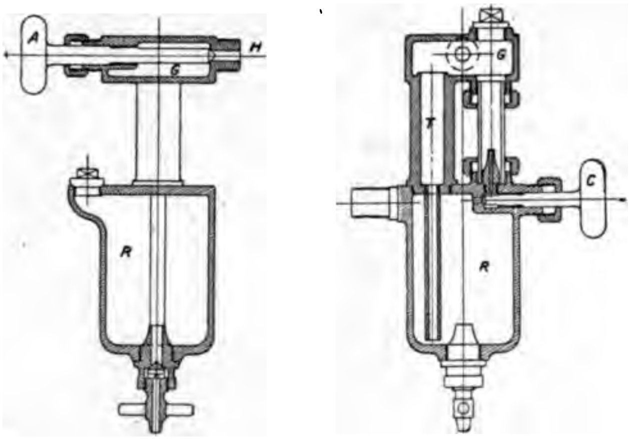

FIG. 116.

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* R. M. Deeley, Eng. Patent No. 7281. (1892.)

water, it forms drops, which rise up the centre of the glass. The rate of feed remains constant, however much the conditions of running may vary. This makes the lubricator very suitable for locomotive work.

There are quite a number of sight-feed lubricators in which a head of water is the motive power, and most of the arrangements are so specialized that they are only suitable for certain kinds of work.

There are other lubricators of the sight-feed pattern, in which the oil is supplied by the pressure of a spring on a piston. There are also a number of cylinder lubricators more suitable for large than for small engines, and so designed that a piston, actuated by a ratchet driven from the engine cross-head, delivers at each stroke of the engine a definite quantity of oil.

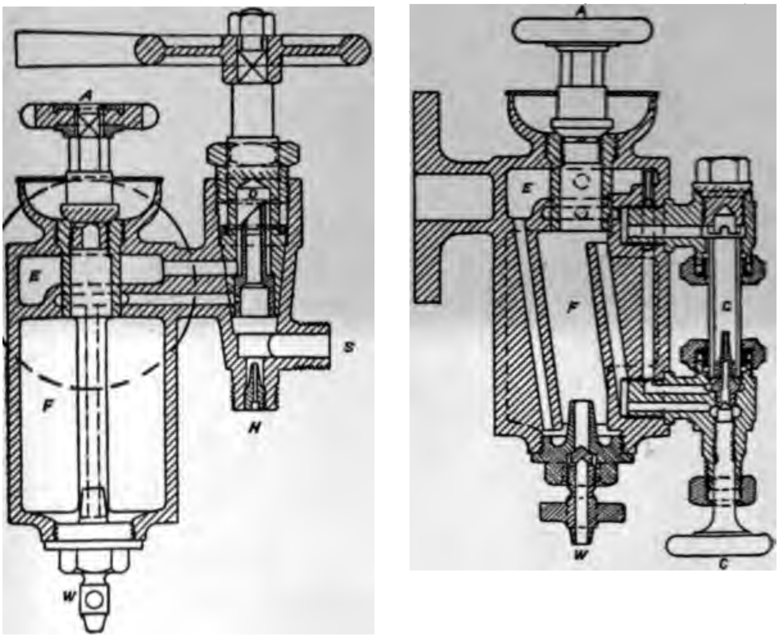

FIG. 117.

In the case of locomotives, the steam has often to be shut off, and the engine allowed to run for long distances without steam. When working in this condition, there is often too little steam passing through the lubricator to more than partially lubricate the engine parts. To prevent any serious injury to the rubbing surfaces under such conditions, lubricators are placed on the cylinders. The most commonly used design is known as the Furness * lubricator, a section of which is shewn in fig. 118. Oil is placed in the bell-shaped chamber, from whence it feeds through the wick or wire gauze cup into the central passage, which it fills. So long as the steam pressure remains in the cylinders, the small valve shewn remains closed, but immediately steam is shut off, a vacuum is formed, the valve is drawn off its seat, a charge of oil enters the cylinder, and so long as the steam remains off, the oil is slowly fed.

To secure lubrication whilst the steam is shut off, the stream of oil and steam coming from the sight-feed lubricator is, in Smith's design, reinforced by a jet of steam, which, by an air valve, is caused to flow direct from the boiler and open the steam-valve when there is a vacuum in the steam-chest.

Design of Cylinders.—To secure good cylinder and valve lubrication, it is essential that attention be paid to the conditions which determine whether the oil shall reach the surfaces or not. The greatest enemy to good cylinder lubrication is water. It wets the surfaces where there is any abrasive action, and effectually keeps off the oil. Water may be present in undue quantity, either because it is brought into the steam-chest and cylinder from the steam-pipe, or is unable to escape from the cylinders owing to the positions in which the steam-ports are placed. When water comes from the steam-pipe in any quantity, a separator should be used and the steam dried. This is nearly always done in the case of high-speed engines, such as the Willans engine. To ensure the escape of such water as condenses in the cylinders, the ports should be placed below them, or so low at the side or sides that all the water may drain away with each opening of the exhaust port. Proper drain pipes must also be fixed to the lowest points of the exhaust pipe when it rises to any height, or the water will remain in the pipe to a sufficient extent to keep the cylinders in a wet condition, and so prevent proper lubrication. To get rid of such water as is condensed in the cylinders and cannot get away freely through the main valves, Holt's drain valve has been found very efficient. A section of this valve is shewn in fig. 119.

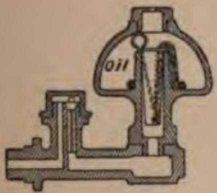

Fig. 118.

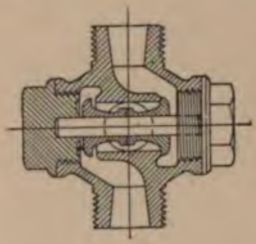

Fig. 119.

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* H. D. Furness, Eng. Patent No. 2437. (1871.)

Here the two valves, which slide freely on a spindle, so control the movements of each other that the one having the greatest steam pressure upon it remains shut and holds the other open. This results in the closing of the drain valve at that end of the cylinder receiving steam, whilst the valve controlling the drain pipes at the end of the cylinder which is being exhausted remains open. Provided that the drain valve is not too large for the cylinders, the water is drained with very little loss of steam, and the bottom of the cylinder, which, in horizontal engines has to carry the weight of the piston, remains well lubricated.

CHAPTER XI.

THE LUBRICATION OF MACHINERY.

Genuineness of Lubricants.—The engineer in charge of a works, factory, or mill, the engineman in charge of a steam, gas, or oil engine, or even the possessor of a cycle or motor-car, although deeply interested in the genuineness and nature of the lubricants he uses, has, as a rule, very limited means at his disposal for determining the nature of the oils, greases, etc., which he purchases. It is no doubt to this state of things that we must attribute the very extensive use of adulterants by manufacturers of lubricants, and the placing upon the market of improperly or imperfectly refined oils.

Makers of sewing and other small machines generally themselves sell the kind of oil most suitable for their lubrication. Such firms are able to obtain a genuine article, and it would be contrary to their interests to allow their customers to use an unsuitable oil. The retail prices charged for such machine oils are, however, so high as to be prohibitive where lubricants have to be used in large quantities, and it is then necessary to purchase from a wholesale dealer, and to take proper precautions to insure that the lubricant is free from adulterants, and suitable for the bearings upon which it is to be used.

The most valuable and expensive oils, such as sperm, olive, and lard, will not always be found pure. Sperm oil is mixed, among other things, with thin mineral oil, and olive with cottonseed oil. The same may be said of lard oil, which frequently contains a large proportion of the cheaper cottonseed oil. Indeed, most of the lubricants are mixtures of various liquids or soft solids, some of which are very injurious. Adulteration, with a view to the thickening of the lubricant, is mainly resorted to in the case of mineral oils; these are also adulterated with rosin oil, and occasionally with neutral coal-tar oil. The sophistication is often very skilfully done, the problem being to add such cheaper ingredients to the more expensive oils as will enable them to pass as many of the tests of the chemist as possible. Attempts are sometimes made to thicken the thinner lamp oils, so as to make lubricants of them. It thus appears that unless the purchaser has some means of ascertaining the true character of [illegible] he has little or no guarantee of its [illegible]

[illegible] has been made of late years in the quality of [illegible]. By improved methods of refining, less [illegible] and the lighter fractions are more [illegible] thus making the various [illegible] in their composition.

Simple Tests for Adulterants.—In the majority of instances, the [illegible] has no means of obtaining an [illegible] of the oils supplied to him, [illegible] analytical chemist versed in the methods [illegible] for many of the adulterants used require [illegible] their presence. In Chapters VI. and VII. [illegible] of the chemical and physical methods [illegible] of adulterants have been described in full. [illegible] by a skilled analyst in a properly [illegible] of the tests, however, can be made with [illegible] and these the engineer should make himself [illegible] they will furnish some very valuable information [illegible] properties of the lubricants offered to him. [illegible] test for free acid is one of these (p. 206). A [illegible] can be made in a stoppered 50 c.c. [illegible] 15·4 c.c. (= about 14·1 grms.) of the [illegible] The cylinder is filled up to the mark with [illegible] phenolphthalein solution is added, [illegible] from a burette, until, on shaking [illegible] The number of c.c. of caustic soda [illegible] approximately, the percentage of free [illegible] the test mixer, and the burette [illegible] for a few shillings from any dealer in [illegible] litmus paper in the oil, as [illegible] useless test. Another easily made and [illegible] watch-glass test for gumming properties [illegible] carefully measured instead of being weighed, [illegible] the *same conditions* with a standard [illegible] may be gained. The watch-glasses [illegible] in any suitable hot situation protected [illegible] the hot air or water-oven can be dispensed [illegible] it is not worth the trouble and time to [illegible] of the adulterant used, the tests being [illegible] whether the sample examined is fit [illegible]

[illegible] in the light of the results obtained with his [illegible] the engineer in most cases to detect the cause of [illegible] When the quantity of oil, grease, etc., [illegible] necessary to have analyses of the lubricants [illegible] by a competent analyst, in order to make sure that they are suitable for the purposes required, and are equal in quality to the sample offered, or that they comply with the specification. (See Chapter VII. pp. 295–318.)

Qualities and Properties of Lubricants.—*Acidity.*—Although animal and vegetable lubricants differ from mineral lubricants in their chemical constitution and activities, in many of their physical properties they closely resemble each other, and it is to these common properties that they owe their lubricating values. Of these properties, viscosity, and oiliness or greasiness are the most valuable. But it frequently happens that an oil which would otherwise be a good lubricant fails to be of practical use owing to its having been allowed to become acid, or to its property of taking up oxygen from the air and becoming thick, either evaporating entirely at ordinary temperatures or leaving a gummy, sticky mass behind. These properties have been dealt with in detail in previous chapters, and need only be referred to here in so far as they concern the use to which the lubricants may be put.

Gumming.—Many oils when exposed to the atmosphere as thin films on bearings rapidly thicken by oxidation, and finally form gum- or varnish-like masses, which clog the moving parts and cease to act as lubricants. A high temperature considerably hastens the rapidity with which this takes place. Gumming oils, such as rape, should not on this account be used in warm places, as they rapidly become thick, clog the trimmings, and considerably reduce the speed of flow through them to the rubbing surfaces.

In places where animal or vegetable oils which are liable to gum have to be used, great care must be taken to prevent the accumulation of waste or other fibrous material saturated with them from being placed near steam pipes, or stored in closed cupboards. Such material should be kept in iron bins in the open air, for in the process of oxidation or slow burning which accompanies gumming, heat is evolved in such quantity as often to set fire to the whole mass. Mineral oils, which are devoid of this property, should be used in theatres, hotels, and other large buildings where the risks of fire are great, either alone or mixed with fatty oils which gum only slightly (see p. 268).

To clean machines which have become covered with a gummy oxidized lubricant, the parts should be well moistened with paraffin oil, which dissolves the gum, allowed to run for a few minutes, and then wiped dry and clean before being oiled again.

An old-fashioned test, now superseded in the laboratory, is that of Nasmyth. A plate of iron or steel, 6 feet long by 4 inches wide, has six longitudinal grooves planed in the upper side. It is placed upon a bench or shelf, in a warm situation as free as possible from dust, slightly inclined, one end being supported on a block 1 inch thick. An equal number of drops, measured from the same pipette, of each oil to be tested and of a standard sample, is placed successively in one of the grooves, and the behaviour of the different oils is observed from day to day. Those of least viscosity will, at first, flow *most rapidly down the* incline, but oxidation or any other cause tending to thicken the oil will gradually arrest the motion, and the effect after a few days will become marked, the best oil flowing the greatest distance.

All animal and vegetable oils, greases, fats, etc., as well as mineral oils, contain acid constituents which will attack the metallic surfaces of bearings, and form soaps of iron, copper, etc. The tendency they have to become more acid with age is very slight in most cases. The extent to which lubricants may be expected to contain acid constituents, and the best methods for their detection, will be found in Chapter VII. page 201.

The temperature at which an oil flashes when a light is brought near its free surface is called the *flashing-point*. This property has been fully discussed in Chapter VI. page 178. No lubricating oil which flashes below a temperature of 340° or 350° F. should be used for indoor machinery without special precautions being taken to prevent risk of fire.

Freezing.—Many oils, which at ordinary temperatures are clear, transparent liquids, become, if the temperature falls sufficiently low, white, opaque, solid masses. Sometimes, as has been shewn in previous chapters, the whole mass of the liquid solidifies at some particular temperature, or certain constituents are thrown down as precipitates; whilst in other cases, as the temperature falls, the liquid becomes more and more viscous, and finally becomes a soft solid. This must be borne in mind whenever bearings are exposed to cold. In such cases the reservoir in which the oil is stored, and the trimmings or other arrangement for supplying the oil in a regulated stream, must be placed close to the shaft, so that the heat resulting from a deficiency in the supply of the lubricant may cause it to flow again, if, by chance, an oil which easily solidifies should be used.

Greasiness and Oiliness.—When a grease is rubbed between the fingers it will be found that they slide freely over one another even when they are pressed together with considerable force. A similar effect is produced when a greasy finger is rubbed over a sheet of glass or other smooth solid. This arises in great measure, if not wholly, from the fact that the grease is not a liquid or viscous substance, but a plastic or very soft solid, which cannot by pressure alone be wholly driven from between the surfaces. On the other hand, the soft solid is easily sheared, the resistance offered to the sliding of particle over particle being very small. This property of greases causes them to form very thick lubricating films even when the loads are heavy and the speeds moderate. At higher speeds, however, they do not compare favourably with the oils, the frictional resistances being much greater.

Except for special bearings, greases are now giving way to blended oils, for the high coefficient of friction and resulting loss of engine power is by no means compensated for by the decreased cost of the lubricant.

Greases are generally made by mixing with a fat or fatty oil alkaline bodies, such as lime or soda. With the addition of water they form soaps, and the mass is easily emulsified. In some cases solids, such as black-lead, French chalk, mica, and gypsum are added. A number of these lubricating greases are described in Chapter V. page 121 *et seq.*

The corresponding property in the case of liquids, which prevents the lubricant from being easily pressed out, is called oiliness. Different liquids possess this property in very different degrees. Thus, although sperm oil is much less viscous than glycerine, it will be found to be a much better lubricant. The glycerine feels harsh between the fingers, whilst the sperm oil feels smooth and greasy. The viscosity of an oil, therefore, by no means furnishes us with an index of its lubricating value. With high speeds, moderate loads, and good lubrication, it is no doubt the degree of fluidity which principally determines the value of a lubricant for any particular purpose; but when the speeds are slow or very high, the loads great, or the lubrication imperfect, oiliness plays the most important part in the reduction of frictional resistances. (See Chapter III. on Superficial Tension.)

The property of oiliness is generally possessed most markedly by the animal oils, less so by those of vegetable origin, and least of all by some mineral oils. It is on this account that the fatty oils are so frequently added to mineral oils, for they give to the latter just that property in which the latter are most deficient.

No simple laboratory test has yet been devised for ascertaining the comparative *oiliness*, or carrying power under heavy loads and at low speeds, of lubricants. Such information is generally obtained by means of mechanical oil-testing machines. However, the value of the results they give, considered from this point of view, varies with the speed, load, and method of oiling adopted—matters which are as fully discussed in Chapter IX. on the Mechanical Testing of Lubricants as our present knowledge seems to warrant.

Viscosity.—Upon the viscosity or degree of fluidity of the lubricant depends the resistance it offers to the motion of the rubbing surfaces of quick-running machinery, and also, in some measure, the loads which bearings will carry at ordinary speeds without suffering abrasion. Each particular animal or vegetable oil has a viscosity which does not vary greatly in different samples, and may be regarded as being in some measure an indication of its purity or genuineness. The viscosity, therefore, need not be specified when ordering, but should be determined for the purpose of ascertaining probable purity. Mineral oils, however, having a great range of viscosities, may be purchased, and it is necessary to state in all cases the degree of fluidity required.

The viscosities of all lubricants vary very considerably with changes of temperature. Thus an oil which, as long as the journal runs cool, is sufficiently viscous to carry the load properly may become so fluid, if the temperature should rise from any cause, that the rubbing surfaces close together and cut and tear each other. The variability of the viscosity of a lubricant with change of temperature is often so [illegible] which works well in a cool place may be altogether [illegible] hot engine-room or warm climate. Castor oil, while [illegible] bearings in England, is, on the other hand, [illegible] where it answers well. Mineral oils vary more [illegible] of temperature than do fatty oils. On this [illegible] of a bearing lubricated with a non-fatty oil going [illegible] worse are great, and they need more careful attention.

[illegible] and nature of this property are fully dealt with [illegible]

[illegible] The lubricants used for the bearings of textile machinery [illegible] by the rapid motion of the spindles, [illegible] upon the cotton or woollen goods, produce more [illegible] stains. Every care is, of course, taken to prevent [illegible] of the lubricant, but as it cannot be altogether [illegible] spoil the appearance and reduce the market [illegible] care is taken to only use those lubricants which [illegible] such as give stains which are easily [illegible] The mineral oils, it would appear, all produce objection[illegible] difficulty be wholly removed, for they sink [illegible] with them the fine metallic powders ground [illegible] even though the oil be clean and [illegible] and be apparently completely removed in the [illegible] changes the metallic powders undergo sooner or [illegible] produce stains of various colours in the [illegible] produced by the oil thrown from heated [illegible] difficult to remove, especially if the [illegible] stock for two or three months. When [illegible] fabric is often found to have become [illegible] appearance where the stain had been.

[illegible] are much less liable to produce [illegible] saponifiable, they are almost wholly [illegible] processes the fabric has subsequently [illegible] mixed from 25 per cent. to 30 per [illegible] any marked effect upon their [illegible] proportions, however, the results are [illegible]

[illegible] depends upon the metals of which the [illegible] produces a red stain, whilst copper [illegible] black.

[illegible] one of the most effective methods [illegible] cotton goods is to impregnate [illegible] allow half an hour for [illegible] the stained part, and then boil the [illegible] hours. Olive oil is more [illegible] before boiling, the fabric is well [illegible] alkali, the mineral oil stains [illegible] removed than when boiled in the kier [illegible] finished fabrics which cannot be wetted again, benzine or benzoline, which dissolve the mineral oil, can be used.[*] The solvent should be applied first in a ring all round the spot, and gradually brought nearer to the centre, and a fibrous substance, such as blotting-paper, used to absorb the oily solution which is driven to the centre. If the solvent be applied to the oily spot direct, the grease is caused to spread into the fabric.

Blended Lubricants.—*Mixed or Blended Oils.*—Mineral oils being much cheaper than the better class of fatty oils, and as, at the same time, they possess valuable properties which they confer upon other lubricants with which they are mixed, the use of blended oils has now become common. Indeed, quite apart from the pecuniary aspect of the case, the blended oils are for many purposes superior to either pure fatty oils or pure mineral oils. The percentage of mineral oil permissible varies according to the load, speed, etc., for, unfortunately, many, if not all, mineral liquid lubricants are deficient in the property we have called *oiliness*, and can seldom be used quite pure. Indeed, at one time mineral oils were regarded with great distrust both by chemists and engineers, and when found mixed with fatty oils they were regarded as objectionable adulterants. The reverse now seems to be the view often taken, fatty oils being sometimes looked upon as adulterants when found mixed with mineral oils. This view seems to have arisen from a conviction that the lubricating value of an oil is wholly due to its viscosity, and that as mineral oils can be prepared of any desired viscosity, fatty oils could be wholly dispensed with. Oils were consequently placed upon the market which were stated to be free from fatty oils, and were sold as pure mineral oils. They, however, proved to contain on analysis a proportion of fatty oil—in other words, they were really blended oils.

In the majority of instances these mixed oils answered admirably, a fact which served to strengthen the view that, from a frictional point of view, viscosity was the property which determined the value of an oil. But chemical analysis was not slow in proving that these so-called pure mineral oils really contained fatty oils, and that it was largely owing to the presence of these fatty constituents that the good results obtained in practice were due. More rational views are now coming into vogue, and users of lubricants are beginning to recognize the fact that the best lubricant for any particular purpose can only be obtained by the careful blending of animal and vegetable oils, fats, or waxes with pure mineral oils.

The following broad principles can, in the absence of more accurate knowledge, be laid down.

Fatty oils act best at great pressures, mineral oils at light pressures. On the other hand, viscid oils give the best results at low speeds, and thin oils at high speeds.[†]

Pure mineral oils are only suitable for pressures below 70 lbs. per square inch when the methods of lubrication are 'perfect' and the metals in contact are such as do not readily seize each other. With increasing loads, the proportion of fatty oils it is desirable to add must also increase, if satisfactory results are to be obtained as regards friction and wear. By increasing the viscosity instead of adding a fatty oil the friction is sure to be increased, even though the rate of wear of the rubbing surfaces may be reduced, and more power is wasted than the economy in fatty oil warrants.

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[*] Pentecost, *Jour. Soc. Chem. Ind.*, 1897, p. 409.

[†] Any pressure below 70 lbs. per square inch may be regarded as a light load, and any speed below 100 feet per minute a low speed.

From the chemical point of view there are good reasons for mixing as large a proportion of mineral oil with any fatty oil as will not interfere seriously with its load-carrying properties. By such admixture, the tendency to gum is much checked, the oil remains fluid, and cotton waste saturated with it is much less liable to fire spontaneously.

As bearing upon the changes which take place in blended oils when used over and over again for long periods, the following results may be here given. The oil in the first column, marked 'new,' is a blended oil used to lubricate the 'blower' of the Thomson-Houston dynamo. The same oil is used to lubricate the armature bearings. The oil in the second column, marked 'old,' is some of the same oil which had been used for the latter purpose, filtered, and used again, for a period of 6 months.

	New.	Old.	Rape Oil.
Relative viscosity at 60° F.,	308	315	410
Relative viscosity at 100° F.,	98	100	158
Specific gravity at 60° F.,	0·9026	0·9030	...
Total fatty acids,	5·83%	6·82%	...
Free fatty acids,	0·28%	0·42%	...
Difference ; equivalent to neutral fatty oil,	5·84%	6·73%	...
Mineral oil,	94·16	93·27	...

The above results shew that by continued use there had been a loss (probably by evaporation) of mineral oil, and a consequent increase in the percentage of fatty oil. This change had resulted in a slight increase of viscosity and of specific gravity. The fatty oil had undergone some oxidation resulting in a lowering of the melting-point of the fatty acids and a darkening of the colour, also a slight, but only very slight, increase in the percentage of free fatty acids.

Animal and vegetable oils cannot, however, be added to all mineral oils with impunity. Solid hydrocarbons, for instance, are present in some mineral oils, which, when they are mixed with vegetable oils, may separate out as a precipitate, and cause trouble by clogging trimmings, lubricating valves, etc.

We have seen that much is to be gained both in economy and efficiency by mixing in suitable proportions mineral oils with fatty oils. Quite a number of these blended oils are placed upon the market, many of them being sold at fancy prices. It is better, however, for the engineer to purchase the pure lubricants he requires, and to blend them himself to suit the conditions under which they are to be used.

Fats and Greases.—The contrast in lubricating properties between mineral and fatty oils exists equally in the case of a pure mineral grease like vaseline and an animal fat such as tallow, the latter possessing in a far greater degree the property of greasiness. In the case of purified vaseline this is due partly to the fact that the excessive refining tends to remove those constituents of the crude oil upon which the lubricating property depends. Thus some of the best mineral cylinder oils, which are excellent lubricants, are obtained from the same crude oil as vaseline.

A large number of lubricating greases are made by incorporating or emulsifying animal and vegetable fats with soap and water, also by thickening mineral lubricating oils with soap. Some of these are described in Chapter V. p. 120. Large quantities of these greases are used, with very good results, for the lubrication of railway wagon axles, and some of them are excellent lubricants for the bearings of slow-moving machinery. When the loads to be carried are exceptionally heavy, solids such as plumbago and soapstone are sometimes added to the grease. These solids prevent abrasion at points where the pressure forcing the surfaces together is very great.

Except in special cases, greases should not be used for quick-running journals, shafts, or spindles, the frictional resistance which they offer to the relative motion of the surfaces causing great loss of power. Thus a case is mentioned by Simpson in which the owner of a mill using water power decided to use grease as a lubricant instead of oil, but owing to the increased friction, the change in the method of lubrication caused the water power to be insufficient to drive the machinery, and the use of oil had to be reverted to. Prof. Woodbury used oil for one of the two rows of looms in a cotton mill, and for the other a consistent fat. He found that, under the same running conditions, the temperature of the bearings lubricated with oil was only 4° higher than the temperature of the room, whereas the temperature of the other bearings was 22° higher. With soap-thickened mineral oils there is the liability of separation taking place, especially under the influence of steam or moisture. The mineral oil runs away and leaves the soap in the grease-box or on the bearing, which is apt to run hot in consequence.

In the case of fats and greases whose melting-points are not much above the temperature of surrounding objects, it generally happens that the lubricating films are so warmed by the friction of the bearings that they actually melt when drawn between the rubbing surfaces and act as oils.

Although unsuitable, on the whole, for moderately quick-running machinery, greases answer admirably in cases where the speeds are low, or where a low coefficient of friction at starting is essential. The cheaper greases, made with rosin oil and lime, are used for cart and truck axles, whilst those composed of lubricants of superior quality are made for railway wagons, pedestals, etc.

Being soft solids (pp. 375 and 386), special methods have to be provided for their application to the bearings, for they do not liquefy as long as they are kept moderately cool. For railway vehicles only the better classes of greases are used, and as friction is an important consideration, the ingredients are in some countries changed to suit the seasons, for a grease sufficiently thick for summer might be altogether too stiff for winter temperatures (see p. 123).

It is well to bear in mind that it is only when the speed of rubbing is low that economy results from the use of greases. At all ordinary velocities a marked increase in the friction is brought about by them. This loss of power is seldom estimated at its true value. As a matter of fact it may greatly exceed the gain resulting from the use of the cheaper lubricant.

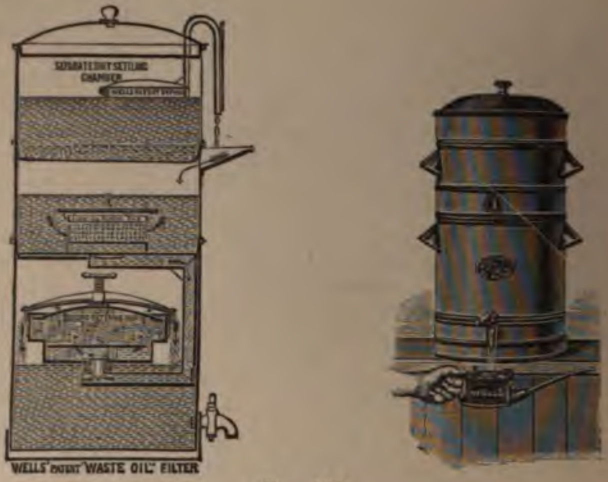
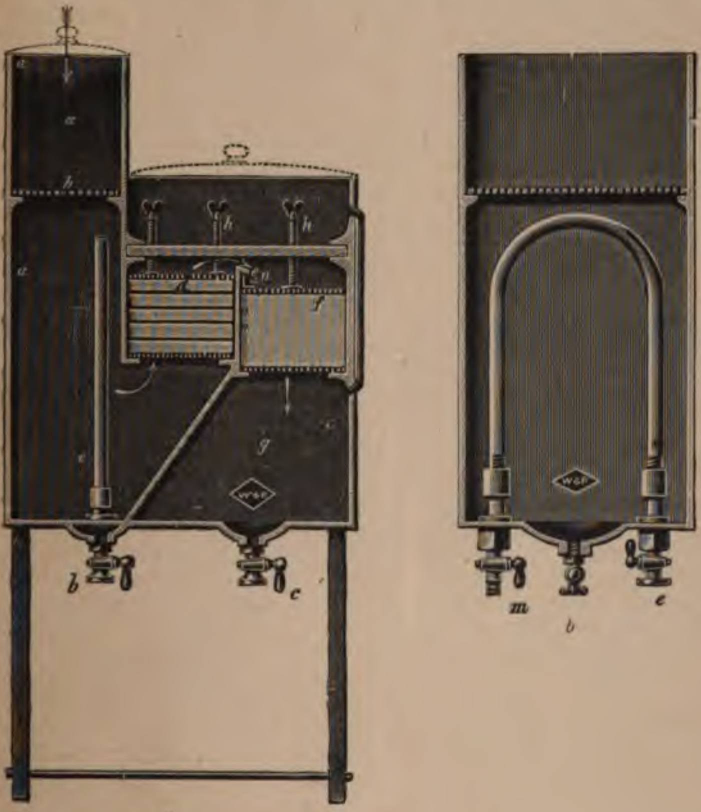

SEPARATE DIRT SETTLING CHAMBER
WELLS' PATENT "WASTE OIL" FILTER

Fig. 120.

Clarification of Lubricants.—*Oil Filters.*—As pedestals, worm-wheel cases, spindle bushes, and various other descriptions of bearings are now frequently made to hold comparatively large volumes of oil which bathes all the rubbing surfaces, or dishes, into which the surplus lubricant runs, are placed below the ordinary forms of bearing, a good deal of oil which was formerly lost is now collected. Such oil contains finely suspended matter of various kinds, and is thick and muddy. Being, in the majority of instances, blended with mineral oils, which do not become changed in character, it is possible to filter out the suspended matter and use the oil over again, for, as a rule, the only change which has occurred is a slight increase in the viscosity, due to the evaporation of mineral oil. In this way all loss of lubricant, other than that resulting from evaporation and some unavoidable waste, is guarded against, and the greatest possible economy secured.

The suspended particles are mostly very fine, and, being immersed in a fairly thick liquid, are not easily removed.

A filter (fig. 120), made by Messrs. Wells & Co., effects this separation of the solid matter from the oil in three stages. The muddy oil drawn from the reservoirs and contained in the oil pans is placed in an upper settling chamber, in which the heavier particles slowly subside. From this chamber the oil is drawn off by means of a siphon pipe, which floats on the surface and slowly removes the clear upper liquid, passing it into a chamber containing a filter, in the coarse mesh of which the larger suspended particles are left. It finally runs into a finer filter pad, through which it is forced by a head of oil several inches or feet in height, as the case may be, and passes into a lower



a

FIG. 121.

chamber, from which it can be drawn for use. The filter pads are readily changed or cleaned.

A filter of different pattern, of which *a* and *b*, fig. 121, are sections, is supplied by Bertram Thomas. The dirty oil is placed in the chamber *a*, to the bottom of which water, dirt, etc., gravitate. The oil having freed itself from the coarsest and heaviest impurities, forces itself slowly through the chamber *d* which has been filled with compressed new twist (preferably white unbleached), rises over the partition *e*, and then filters through the chamber *f*, also filled with compressed twist, into the chamber *g*, from which the clean oil can be drawn off through a cock. It is necessary to heat the oil to 140°–212° F., according to its consistency. This is done in the lower part of the chamber *a* by means of a coil *e*, through which steam can be passed from the engine mains as desired.

Grit, etc., in Oil.—Before rejecting any particular lubricant because difficulty has been experienced owing to the heating of the bearings supplied with it, care must always be taken to ascertain whether the fault really lies with the lubricant, or with impurities accidentally introduced. Enginemen are apt to think that a certain number of hot bearings are sure to occur, however careful they may be. No doubt, even when the greatest care is taken, bearings will occasionally run hot. But in all such cases the heating must arise from some irregularity, and the extent to which trouble is experienced is, in the majority of instances, a measure of the capacity of those in charge of the machinery to keep things in good order. Thus, as an instance, although the quality of the oil used may be excellent and very suitable for the purpose for which it is being used, still the engineman may be troubled with hot bearings, often, indeed, when extra care has been taken to keep the machinery in good order by giving it an ample supply of oil. This almost always arises from the presence in the lubricant of mechanical impurities, such as sand, sawdust, glass, vegetable fibre, mucilage, or precipitated paraffin wax. In transparent oils these are easily seen, but in the thicker dark varieties they are almost entirely invisible. When oil containing such impurities, which it very commonly does, is poured into oil cups in the usual way, the solids are filtered out by the trimmings, or settle to the bottom of the reservoir, and do not get into the bearings. But enginemen frequently go round their engines and run a little oil into the ends of the bearings, or even remove the trimmings or oil-pads and pour oil directly upon the bearing surfaces, and thus introduce grit at points where it can easily get between the rubbing surfaces. Films of various kinds also settle on the trimmings, or obstruct the oil passages, and prevent the oil from finding its way with the necessary freedom to the working surfaces.

Straining of Oil.—In most engine-houses the different oils required are stored in iron tanks, from which they can be drawn as required. Into these tanks the lubricants are pumped from the barrels supplied by the oil merchants. To enable as much of the oil to be removed as is possible, the pump pipe is passed through the bung hole and reaches to within a very small distance of the barrel bottom. The oil, as it is drawn out, thus carries with it the greater part of any solid material which may lie there. To prevent such foreign matter from passing into the oil tank, a receptacle made of fine wire gauze should be fitted into the man-hole of the tank in such a manner that it can without difficulty be taken out and cleaned.

To still further reduce the risk of small particles of grit entering the oil can, the lubricant as it is given out for use should be carefully strained through wire or cotton gauze as it is drawn from the tanks; for, however good it may be, the fine solid particles it sometimes contains, if, as we have seen, they should chance to be introduced between the rubbing surfaces, will give rise to excessive friction, cause overheating, and make the engineer feel uncertain whether he is using a suitable lubricant or whether his supply is really up to sample.

When the loss which may result from the stoppage of the engines driving a large mill or ship, or generating current in an electric installation, is taken into consideration, this double precaution, adopted to prevent the introduction of solid matter, does not seem uncalled for.

Grit is also found in solids, such as graphite. As such solids mixed with fats are sometimes used to put upon bearings which have suffered abrasion and become overheated, its presence may quite defeat the purpose for which the solid was applied.

Lubrication of Bearing Surfaces.—*Lubricants for Low Speeds* (*i.e.*, below 100 feet per min.).—When the relative speeds of the rubbing surfaces are less than 10 feet per minute with perfect lubrication, or about 100 feet per minute with siphon lubrication, the lubricant, instead of being forced between the journal and brass and parting them, is rather swept on one side; the lubricant then depends for its efficiency almost wholly upon its oiliness. As the actual loads bearings will carry under such conditions without seizing depend largely upon the nature of the surfaces in contact, as well as on the oil used, it is not possible to give more than very general figures. The relative carrying powers of oils, greases, and solid lubricants can, however, be approximately stated, and the engineer must in each case by actual trial select that which gives the least amount of heating and friction.

Dealing in the first instance with those lubricants which have the greatest carrying power we have—

(*a*) Graphite, soapstone, and other solid lubricants used dry. Their efficacy depends largely upon the nature of the rubbing surfaces. Graphite, for instance, gives the best results when used on cast-iron surfaces, which are naturally somewhat porous. When these lubricants will not keep the bearing cool, the liberated heat must be carried away by a continuous stream of cold water passed over it, or through perforations in the metal. The wear and loss of power under such conditions are very great.

(*b*) Solid lubricants mixed with greases made from lard, tallow, vaseline, etc., or rosin grease. These mixtures are very suitable for heavy work, especially when metal works against wood. They are largely used for all kinds of rough work, such as cart-axles, tip waggons, hauling machinery, etc., give a small coefficient of friction at low speeds, do not waste away very rapidly by evaporation, and do not run off the bearings, leaving them dry.

(*c*) Axle greases composed entirely of soft solid, and liquid lubricants emulsified with water and alkaline compounds to neutralize acidity. These greases are excellent lubricants for all slowly-moving shafts and journals which have to carry considerable loads. Even for railway waggons they are largely used; for the frictional resistance is small at low speeds, and trains lubricated with them are easily started.

(*d*) Fixed oils such as lard oil, neatsfoot oil, olive oil, rape oil, castor oil, etc., must generally be used pure if the load exceeds 250 lbs. per square inch. Indeed, in some cases, when the pressure is never relieved, even these loads cannot be carried unless one or other of the surfaces be exceedingly hard.

(*e*) Blended oils, *i.e.*, mixtures of fatty oils with mineral oils, can only be used with moderate loads, and, as the latter increase, the proportion of fatty lubricant must also increase, or the wear will be excessive.

Lubricants for Moderate Speeds (*i.e.*, above 100 feet but below 400 per min.).—At speeds exceeding 10 feet per minute for perfect lubrication, and 100 feet per minute for more or less imperfect lubrication, a lubricant, in the case of a journal or shaft, forms a fairly thick film which wholly or almost wholly separates the rubbing surfaces. The conditions under which this film forms have been fully dealt with in the chapter on The Theory of Lubrication (p. 49). It may be mentioned, however, that when the loads are moderate (200 lbs. per square inch, or even more when the lubrication is perfect) the friction and also the formation of the film are wholly due to the viscosity of the liquid. But with heavy loads the bearing surfaces are brought into contact at a point on the 'off' side of the brass, and when this is the case a liquid possessing oiliness to a marked degree is required to prevent seizing.

In the case of plane surfaces, such as slide-blocks, viscosity is not quite so important a property from a lubrication point of view as oiliness, and unless the loads be small (70 lbs. per square inch or thereabouts), a good fatty oil must be used.

In selecting a lubricant for journals running under ordinary conditions of speed, greater attention should be paid to viscosity than to any other property, provided always that the loads do not exceed 200 or 250 lbs. per square inch; for, by making the bearing surfaces of suitable materials, little harm will be done by the contact of the rubbing surfaces during the short slow-speed intervals of running. The lubrication must, however, be as perfect as possible. Indeed, it is owing to the imperfect lubricating devices so largely in use that expensive fatty oils have to be used in place of the cheaper mineral ones. These expensive oils are somewhat apt to become acid or to gum, but in reservoir bearings carrying heavy loads, and properly designed to give perfect lubrication, the objectionable qualities of the fatty oils it is necessary to use are masked by an admixture of mineral oil. Indeed, this form of bearing reduces the friction to the smallest possible figure, enables a cheap oil to be used, and economizes the lubricant.

For bearings carrying small loads pure mineral oils answer admirably, the viscosity selected being the smallest that will enable the oil film to form properly. On the whole the lower the speed the greater should be the viscosity, and the higher the speed the smaller the viscosity. This applies with special force to mineral oils. With increasing loads, especially if the lubrication be imperfect, it will be found that considerable wear and overheating will result unless fatty oils be added; but it is only in exceptional cases, such as when the lubrication devices are poor, that pure fatty oils need be used alone. For locomotive engine work, about 30 per cent. rape and 70 per cent. mineral oil will generally work well.

Except in special cases, greases should not be used unless mixed with a good mineral oil, the oiliness of which they increase.

The bearings of railway vehicles are somewhat exceptional. They have to carry loads of as much as 380 lbs. per square inch, and often run at journal speeds of 9700 feet per minute, as well as very slowly. On this account, great care has to be taken in their lubrication and design. The bearings are made of white-metal or bronze, are long and narrow, are well lubricated by a pad placed beneath the journal, and are kept cool to some extent by the rapidity with which they pass through the air. With bronze bearings, only about 33 per cent. of the best mineral oil mixed with 67 per cent. of olive oil can be used without danger of trouble at high speeds.

Lubricants for High Speeds (*i.e.*, above 400 feet per min.).—Quick running spindles, dynamo shafts, and, indeed, all kinds of high speed bearings, require ample bearing areas and thin oils for their lubrication. The loads carried per square inch are consequently low, and pure mineral oils may be used with advantage. There are instances, however, where good lubrication is impossible, and to minimize the wear a good fatty oil must be used. The bearings for such speeds should always be so constructed as to keep the surfaces well supplied with oil without wasting it. When this is done, mineral oil containing about 10 per cent. of fatty oil answers admirably, for there is then little wear, and the frictional resistance is small.

Lubrication of Miscellaneous Machines.—The spindles of small machines, such as clocks, watches, and other delicate mechanisms, are generally of hard steel. They work either in agate or other polished mineral bushes, or upon hard brass or bronze. The speeds are generally slow and the lubrication imperfect. The pressures are also small, generally only a few pounds or ounces per square inch. The smaller spindles are carefully moistened with a fatty lubricant and put into position. The spindles then have the capillary spaces between them and their bearing surfaces filled with oil, which must [illegible] without renewal and be non-corrosive. [illegible] from the solid fat, carefully [illegible] olive oil are the best for [illegible] commercial oils of these kinds cannot be [illegible] analysis has proved them genuine [illegible] method of testing small quantities of oils is [illegible]

[illegible] watches, and such small machines requires [illegible] there is no alternative, it should [illegible] an expert.

[illegible] similar machines, a mixture of [illegible] per cent. of mineral oil works [illegible] all work under heavy [illegible] speeds, for the slip of the [illegible] and their bearing surfaces is very [illegible] which slip takes place in such cases and [illegible] can thus be explained by the theory of [illegible] Chapter I., page 13). Here we are [illegible] wear than friction, and such friction as [illegible] a good fatty oil, pure or mixed [illegible] the most suitable. The chain of a cycle, [illegible] of the pins and of the links on the teeth [illegible] which require a good grease or a [illegible] with a little vaseline to thicken it, [illegible] from [illegible] if they should [illegible] Excellent results are also obtained [illegible] of pure sperm oil, which is held [illegible] Pure mineral oils seem [illegible] bearing surfaces are apt to wear [illegible] a thick oil or grease is [illegible] rapidly runs off. If properly [illegible] lubricated, a cycle chain [illegible] more than once or twice in a year.

[illegible] many of the rubbing [illegible] a great measure bathed in [illegible] for them must be carried by [illegible] over and over again, mixed [illegible] to meet the waste due to [illegible] the tank from which it is [illegible] from the machines. In such [illegible] the best lubricant, but a little [illegible] The soap formed in or added to [illegible] surfaces with which the fluid comes [illegible] films which prevent the cutting [illegible]

[illegible] from street mains, and is passed after [illegible] is generally added drop by drop by [illegible] mechanically by the hydraulic machine.

The rate of supply is thus regulated in accordance with the volume of water passing. When the pressure is below 750 or 800 lbs. per square inch, a mixed mineral and animal oil answers well, but for higher pressures soft soap is a better lubricant. Hydraulic rams, slides, guides, etc., in cool climates may be lubricated with tallow, provided it be free from acidity, as this lubricant does not alter much at ordinary temperatures.

Solid Lubricants.—Many solid substances, such as soapstone, graphite, asbestos, etc., are used as lubricants. They cannot easily be squeezed or scraped from between rubbing surfaces, and are, consequently, suitable where very great weights have to be carried on small areas, and where the speed of rubbing is not high. Indeed, some solid lubricants will sustain, without injury to the surfaces, pressures under which no liquid ones would work. As a rule, the bearing surfaces are made of exceedingly hard materials. Between cast-iron surfaces plumbago has been found to give good results. Mr. T. Shaw found it to be superior to oil for the tables of heavy planing machines. For light bearings, such as are found in lace-making and silk-weaving machinery, it is also sometimes used, oil being an objectionable substance in such fine, clean work.

Lubricants for Nuts, Keys, etc.—To enable nuts, boiler wash-out plugs, keys, etc., to be easily placed in position, and removed again after standing, it may be for months or years, in warm places, a lubricant is required which keeps its nature and does not evaporate, corrode, or otherwise injure the metallic surfaces. For such purposes, tallow, or other fat or oil, or greases containing them, should on no account be used. No doubt they make the nuts, etc., work freely in the first instance, but in a very short time the fat undergoes a change which effectually corrodes the surfaces together. Even a mineral oil, although it does not set up corrosion, flows out of the joint in the course of a few hours when heated, evaporates, and leaves the surfaces free to 'bind.' To prevent this, the best plan is to make use of a lubricant consisting of a thick mineral oil or petroleum jelly mixed with black lead. Here, even if the fluid or semi-solid portion of the lubricant should be driven out of the joint by capillary forces, the black lead remains in the joint, keeps the nuts, etc., free, and enables them to be easily tightened or taken off at any time without risk of breakage or damage.

However, there are cases where no lubricant must be used, such, *e.g.*, as the nuts of the bolts securing fish plates to rails, which, if lubricated, would be apt to slacken back. The same may be said of the bolts securing many of the parts of machines subject to vibration.

Lubrication of Boiler Fittings.—The valve spindles, valves, etc., of fittings attached to steam boilers are apt to work rather stiffly owing to the difficulty of lubricating them, and the rapidity with which most lubricants leave the heated surfaces. For them the mixture described above for nuts, etc., answers well, the lubricant in all cases being a mineral oil or grease containing a lubricating solid such as black lead or French chalk.

The glands of low-pressure boiler fittings may be packed with hemp or jute soaked in paraffin wax containing French chalk or black lead. *The soft solid lubricant should on no account be a fatty oil or grease.* Such lubricants attack the metallic surfaces with which they come into contact and cause the glands to leak. For high pressures, or in very hot positions, the hemp must be replaced by asbestos cord or metallic packings.

Some enginemen have adopted the practice of putting oil, or the waste water from their lubricators, into steam boilers, either through the injectors or into the feed water. This practice is one which should *not* be adopted under any circumstances, for the acids thus passed into the boilers give rise to or seriously accelerate the rate of corrosion, which often results from the strains set up in the metals by changes of temperature, etc. Lubrication effected in this way not only endangers the lives of those who adopt the plan, but is sure to seriously shorten the life of the boiler, especially if the water be soft. If the water be hard, greasy deposits are formed which are apt to cause over-heating and collapse of flues, etc.

Selection of Lubricants.—Although it is clear that for each kind of bearing, speed, and load, only a comparatively few varieties of lubricants out of the great number placed by manufacturers on the market will be found to give equally good results, in practice the disadvantages resulting from having a large number of oils, etc., in use at the same time is so great that practical men, as a rule, prefer to use a few lubricants only, selected so that they shall answer as nearly as possible for all purposes. This limitation may, however, be carried to extreme lengths, and greater waste of power and damage to wearing surfaces caused than the convenience warrants.

But the advantages to be gained by carefully selecting lubricants according to the kind of bearing to be lubricated are clearly becoming more and more marked as time goes by, for the speeds at which the machines used in textile industries run are becoming greater and greater each year, as are also the loads placed on many of the bearings. The conditions under which lubrication has to be effected are, therefore, rapidly becoming more diverse, and the time when the [illegible] use almost any lubricant placed on the market has [illegible].

The [illegible] selection of lubricants can only be accomplished by [illegible] experimentally the extent to which different oils, etc., [illegible] is often only [illegible]. This the [illegible] will be dealt with [illegible].

Cost and Efficiency of Lubricants.—Although in the selection of [illegible] economy in [illegible]. This will [illegible] be seen when the [illegible] compared with that spent [illegible] it has been maintained with some shew of reason that the consumer can frequently better afford to use the highest priced and best article than the lower priced one free of charge. This is certainly the case with small mechanisms, such as sewing machines, clocks, and the like.

Not only may the loss by friction be largely increased by using an unnecessarily thick lubricant, or the bearings clogged by using a gumming oil, but the wear and tear of the surfaces may become very great and the life of the parts be much shortened by using a lubricant deficient in *oiliness*. It is therefore imperative that the chemical and mechanical, as well as the commercial, aspect of the question should receive careful attention, for many so-called *special oils*, for which a high price is demanded, are really compounded of very cheap ingredients. The experimentally ascertained quality and not the price alone must therefore be the guiding principle in the selection of lubricants.

Management of Machinery.—*Cleanliness.*—One of the first points to be attended to, if machinery is to be kept in good order and work satisfactorily, is cleanliness. We have already pointed out the necessity of keeping grit and dirt of various kinds out of the lubricants used. But rapid wear and even overheating may result from dust blown about the engine or machine room. On this account, proper care should be taken to prevent the accumulation of dust in corners, louvres, etc., for in windy weather it is liable to be suddenly scattered over the machinery. Indeed, every precaution should be taken to prevent the admission of grit and dirt, the floors being moistened and swept repeatedly, and every corner scraped clean. In many cases it is well to cover motors, dynamos, etc., when not at work, by canvas coverings.

The extent to which proper care is taken to keep the machinery in order, and in proper running condition, is nearly always reflected by the general appearance of the installation. Carelessness of management go hand in hand with dirty machinery and untidy engine-houses and shops. In many of our modern engine-rooms, dust, dirt, and scattered oil or waste are considered as much out of place as they would be in a dwelling-house.

The nature of the task imposed upon the engineer in charge of an engine-room or mill depends largely upon the design of the machinery he has to look after. As extreme cases we may contrast the huge, slow-moving pumping engine of the last decade with the comparatively light, high-speed motors furnishing power for a modern electric-light station. In the one case lubrication is generally effected by the old imperfect siphon arrangements, and in the other by the more modern automatic methods giving perfect lubrication. On the score of satisfactory running there is little to choose between the two methods, but the older machines cannot compare as regards first cost and economy with the more modern designs. But it frequently happens that steam, gas, and oil motors are made to run at speeds for which their lubricating arrangements are quite unfitted, and it is only by the exercise of the greatest care that casualties can be avoided. Free lubrication and [illegible] fixed in such a [illegible] placed to [illegible] ends of the [illegible]

[illegible] lubrication [illegible] containing [illegible] undue [illegible]

[illegible] 500 to 15,000 [illegible] confined to [illegible] power, and the [illegible] successfully [illegible] in the oil [illegible] running, [illegible] being thrown [illegible] opposite side to [illegible] either [illegible] by a small [illegible] bearing.

[illegible] only an [illegible] with grease are [illegible] this grease [illegible] prevents for the [illegible] often [illegible]

[illegible]

[illegible] machines are [illegible] lubrication [illegible]

Starting of New Machinery.—To insure the proper working of any such complicated piece of mechanism as a steam engine, especially if it be run at a high speed and with a heavy load on the bearings, or if the work transmitted or developed be large, much depends upon the intelligence of the erecting fitter or of the engineman who sets the machine in motion. Of course the bearings may be so designed that, owing either to the strains set up by the stresses acting on them, or the expansion of the parts from the heating of the cylinders, etc., the rubbing surfaces are pressed together with undue force in places, and cannot possibly run cool without some small alteration being made or additional clearance given. Upon the engineer in charge, therefore, falls the duty of making good such defects in the bearings or their method of lubrication, by giving freedom to certain parts, such as slide bars, to expand so that they may not buckle with changes of temperature, putting in lubricating grooves, etc., where they have been omitted, arranging for the proper escape of condensed water from the cylinders, and taking care that all the surfaces have been properly bedded together. All omissions detected or alterations made should, of course, be carried out with the cognizance of those responsible.

Even when all precautions have been taken, an engine will seldom run cool if it be at once run with the full load on or at its maximum speed. This arises from the fact that for good lubrication, and to obtain a low coefficient of friction, the working parts must bed themselves together in a way which a fitter is quite unable to imitate. Indeed, in a short time all bearings, if properly designed, are worn to a shape which enables the lubricant to be drawn in between the surfaces and wedge them apart. When this shape has once been attained, further wear at running speeds almost ceases, especially if suitable methods of lubrication and proper lubricants be used. The machine should consequently in the first instance be run with a light load at a very low speed. Under those conditions the wear is comparatively rapid, especially if a moderately thin mineral oil be used and the journals and pins be allowed to bed themselves in the brasses. The speed should then be increased, and the blended oil used when, after some hours' running, the working speed has been attained. During this stage it is well to supply the lubricant liberally, to prevent overheating.

In the case of railway vehicles, even when the greatest care is taken, a journal may run hot; it then becomes necessary to change the brass. A hard white-metal or bronze bearing cannot be expected to run well at first, even if very carefully fitted, for the correct form of the surface can only be brought about by wear, and whilst such wear is going on at high speed the heat developed may be very great. To enable a vehicle, a bearing of which has become so hot as to damage the rubbing surfaces, to be run at once, a new brass may be put in with a lead surface about $\frac{1}{16}$ inch thick. This rapidly beds itself upon the journal in such a way as to form a good surface where the journal is smooth, and does not bind heavily where the journal is damaged. A lead surface of this kind, Mr. H. R. Haigh states, will run several hundred thousand miles without being worn off.

Methodical Habits of Lubrication.—The most prolific source of trouble experienced with machinery arises from the occasional failure of the attendant to give each bearing its proper supply of oil. No doubt an unsuitable oil, the presence of grit, or some such cause may easily result in overheated bearings, but as a rule there must be a practically complete failure of the supply to give rise to a casualty. That this may happen very easily will be recognized when the number of bearings to be oiled in some machines is remembered;

[illegible]

[illegible] at stated intervals, [illegible] or there is some [illegible] parts taken to pieces [illegible] were when removed. It is urgent [illegible] for it is impossible to [illegible] gives the least frictional resistance. [illegible] should, therefore, be confined [illegible] "tinkering" with the rubbing [illegible] as possible. Indeed, a well designed [illegible] should run for years without the use of either a file or a chisel, provided it be kept clean and the lubricating appliances be always in good working order.

In dusty or dirty situations, where the oil has a tendency to thicken, or in cases where the wear of the bearing or shaft is considerable, deposits are apt to form in the oil-ways and prevent the proper flow of the lubricant. To prevent such deposits from collecting to a serious extent, pedestal caps, etc., should be occasionally removed and cleaned.

When pad-lubrication is resorted to, it is necessary to remove the pads every few weeks and clean the surface which comes in contact with the moving surface, for the wool often becomes glazed by the metallic surface against which it rubs. The pad must, therefore, be scraped clean and well oiled each time it is removed, *i.e.*, about once a week. Unless this be done regularly and often, the bearing will not keep cool and wear well.

Trimmings also require frequent examination and renewal. In warm places fatty oils gum and clog the pores, as does dirt in dusty places. Want of proper attention to trimmings is a fruitful source of heated bearings, for the volume of oil supplied by them varies with the number of strands or with the fit of the woollen plug in the oil-hole. Any change either in the fluidity of the oil or in the cleanliness of the pores also alters the rate of supply to the bearing.

Where the lubricant is supplied by oil-cups fitted with small valves at the bottom in such a way that the rate of feel may be judged by the rate at which the oil falls from a small nozzle, the passages are apt to become suddenly clogged by mucus or dirt stirred up from the bottom of the reservoir. They should, therefore, be regularly examined and cleaned out. The oil should also be removed periodically from all reservoir bearings, filtered, and, if not too acid, used over again.

Examination Book.—To insure the examinations being really made at the required intervals by those whose duty it is to attend to such matters, an examination book should be kept in which is clearly stated the nature of all periodical examinations, a column being provided for the engineman or fitter to sign after having made each inspection.

The necessity for adopting this course is the greater the larger the station or mill, and the more numerous the machines of various kinds it contains. Such machines, motors, or lines of shafting must be consecutively numbered, so that they may be easily identified and the entries referring to repairs or examinations properly kept up.

If such a book be not kept, the engineer in charge cannot expect each motor, etc., to be properly and regularly attended to, for some portions of the machinery will receive undue attention, whilst others will be neglected, and all sorts of difficulties will arise which a better organized system would prevent.

Preservation of Machinery not in Regular Use.—It frequently happens that an engine plant for the supply of power is put down in duplicate, and parts may have to stand idle for weeks or even months. Whenever possible such engines, etc., should be worked alternately, so that all the surfaces may be kept clean, smooth, and in good condition. When such motors as marine engines have to stand idle in dock, it is well to get up steam occasionally and run the engine for a few hours. Should this be impossible, the engine must be pinched round once each day to keep the cylinder faces in good order. Discs fitted with teeth are often keyed on to the shaft for this purpose.

Grease for Protecting Polished Surfaces.—In cases where the engine or machine is to lie idle for any length of time a better plan is to *take the parts to pieces*, clean *all* the rubbing surfaces, and cover them with a protecting paint. The same treatment should be accorded to accurately machined faces which are to be used for rubbing, and, indeed, all light work which is to be kept ready for use, as soon as it is finished. Unless this plan be adopted, the bearing surfaces will become pitted and rusted to such an extent that the machine will cost more to repair than it is worth.

The most commonly used mixture for this purpose is one consisting of white lead and tallow. It forms a good cover when put on warm and does not corrode the metals, as the acid constituents of the tallow, if there be any, are converted into lead soaps. The white lead in this mixture plays the part of the lime or soda in the numerous axle or other greases.

When the machinery is for export purposes, and may be exposed to rain or moist air, the surfaces must be covered with black enamel or japan, which effectually protects them from rust, even if they should be immersed in water for many hours. A black japan made from oil-gas tar called 'Siderosthen' is very suitable for such purposes, as it forms an unbroken covering film, and does not become brittle with age.

Overheating of Bearings.—We have already mentioned a number of causes which may lead to overheating, which should have been provided against either whilst the machine was being erected or during the preliminary or trial runs. It sometimes happens, however, that a bearing may run short of oil for a few minutes, or that grit may get between the surfaces and cause trouble. When this occurs to a marine engine bearing and the damage likely to be done to the engine is less serious than that which would result from the stoppage of the vessel, it is the custom to turn a stream of water, if possible soapy water, upon the heated parts and keep going. In many cases plumbago thrown over the heated surface, or run on to it mixed with oil, will prevent serious injury. Much the same may be said of a locomotive bearing as regards the advisability of stopping, but here nothing must be done which will endanger the safety of the train. Electric light engines, where they are in duplicate, and most other motors, machine tools, etc., can be stopped for examination at once. Unless this be done promptly, the injury sustained may necessitate a new step or journal.

In all cases of sudden heating it is wise to at once use a good fatty oil, as they do not, to the same extent as mineral lubricants, lose their viscosity with rise of temperature, and are more oily. A can of rape or olive oil may be kept handy for such emergencies.

To run without attention a bearing which becomes heated day after day is a great mistake, as there must be something radically wrong to cause such heating. The shaft or journal may be oval, one or other of the surfaces damaged, grooved, or flawed, the oil-ways blocked up, the footstep distorted by overheating, the lubricator working improperly, the shaft sprung out of line, etc. It might not appear at first sight that a mere crack in the crown of a brass, especially as it scarcely affects the area of contact, would cause trouble. But it must be remembered that such a crack allows the oil to escape, and largely reduces the carrying power of the oil-film.

The real condition of a bearing which habitually heats can only be ascertained by taking the parts to pieces, and when this has been done there is no excuse for not making every defect good.

Bearings which fit too closely are very apt to run hot; on the other hand, those which are too loose make a great noise, and the repeated blows not only tend to produce and develop flaws in the moving parts, but also to damage the surfaces. What should be aimed at is a free bearing in which there is room for the oil-film to form.

Friction and serious heating may be produced by using a lubricant either too low or too high in viscosity. When the viscosity is too low, the oil pressure-film, which keeps the bearings of rapidly moving machinery from touching, does not form properly, and solid friction results. On the other hand, when the viscosity is too great, the frictional resistance of the film is so large that the bearing becomes warm or even hot. That it is best to use an oil having as small a viscosity as possible has been demonstrated over and over again, especially when, as in the case of textile or printing machinery and dynamos, the bearings run at high speeds and the loads per square inch are small. The heat liberated, and therefore the friction encountered, is proportional to the internal friction of the lubricant, and when it is remembered that at high speeds there is a continuous film of oil separating the surfaces, and that the friction in journals and spindles is proportional to the viscosity, it is clear that heating is as likely to be due to the want of fluidity of the lubricant as to actual metallic contact action. The best results are consequently obtained by using lubricants of the lowest permissible viscosity. Yet, frequently, the engineer in charge assumes that the heating results from the rubbing of the surfaces against each other, and is surprised to find that when he uses a thicker oil his bearings become still hotter.

Main engine bearings, the steps of which are separated into several portions, are very apt to run warm. This arises from the fact that to obtain good lubrication each of the brasses should be able to assume the relative positions, with regard to the journal, shewn in fig. 92, p. 364.

When there is only one bearing step, the shaft or journal can place itself in the position necessary to give it carrying power, but, on the other hand, when there are two or three separate brasses, they must have freedom to move into such positions that there shall be a wider gap on the 'on' than on the 'off' side. The degree of freedom required is very small. The best way to secure it will depend in each case upon the adjusting arrangements.

It sometimes happens that a locomotive axle-box bearing, fed with oil through a hole and groove in the top of the brass, will run hot, and continue to do so, although every care has been taken to secure well-fitting faces. Now it has been repeatedly shewn, especially with mineral oil, and, less markedly, with fatty oils, that when the oil is supplied in this way it is unable to properly wet the journal, being scraped off by the closely-fitting edges of the groove. Indeed, the better the fit of the brass and journal, the more the oil is confined and prevented from getting to the proper place, viz., the 'on' side of the brass. As a rule, the side play of the brass enables it to mount on the curves at the ends of the journal, and in this manner the oil is liberated and runs over the journal. A couple of small grooves from the oil-way to the ends of the brass will answer the same purpose and prevent overheating, provided the load be not too great.

A siphon may cease to feed long before the oil reservoir is empty, and may thus mislead. The height to which the lubricant can be drawn from a reservoir by a trimming depends upon the fineness of the material of which it is made. Thus cotton wick will raise the liquid much higher than worsted will. The latter material only lifts lubricating oils about 1¼ inches. Lubricator reservoirs are often made much deeper than this, and if not regularly cleaned out, they gradually become partly filled with a sticky, dirty mass. The better plan is to make them shallow and to clean them out often.

A bearing which habitually runs warm cannot be considered as working properly, even if it never actually heats so badly as to necessitate a stoppage, for the coefficient of friction must be high and the waste of power considerable. Such a bearing has either got too much weight upon it, is not in line with other bearings on the same shaft, or its surfaces are grooved and the oil-film cannot form. When this is the case, the shaft or journal, and also the brass, must be filed or machined to true faces. It occasionally happens that on taking the pedestal cap or brass from a bearing which has begun to get hot, the shaft or journal will be found to be badly flawed.

Efficiency of Lubricants.—By means of the physical tests above enumerated and described in detail, the viscosity, gumming properties, acidity, flash-point, etc., of various lubricants can be ascertained in the laboratory. If it were not for the fact that there is as yet some uncertainty regarding the methods of measuring the comparative oiliness of lubricants of different viscosities, there would be little difficulty in deciding which, of a number of lubricants, was the best to use for any particular purpose. Although mechanical testing machines, if properly used, give us some considerable information on this head, it is only by a knowledge of the extent to which each lubricant keeps the various bearings cool, and reduces friction and wear, that the engineer can judge properly whether he is obtaining the best possible result.

An accurate estimate of the comparative value of different lubricants can only be made by carefully ascertaining the frictional losses each lubricant entails and comparing these losses with the total work done by the prime movers. Knowing the cost of the fuel, etc., used, the engineer can then calculate how much he is expending in unproductive work with varying conditions of lubrication. By occasionally weighing his pedestal brasses, valves, etc., he can also measure the rate of wear going on in his machinery. A knowledge of such points will enable him at once to see whether he is losing or gaining by the adoption of any particular lubricant or lubricants, and also to note the effect produced by changes of temperature. Such knowledge is easily gained by fixing indicators on steam or other motors when all or certain parts of the machinery are running light, also when each machine has its full load, and again under normal conditions. In all cases when the power used is an important item, these observations should be made periodically, the results entered up for future reference, and a balance sheet drawn up so as to enable the cost of power, and also of lost work, etc., to be compared with the expense incurred on lubricants.

Steam Cylinder and Valve Lubrication—*Imperfect Nature of.*—Although it is possible to so lubricate the cylinders and valves of a steam engine that there shall be no excessive wear, it is impossible to obtain anything like the results, as far as friction is concerned, given by a well-lubricated journal. The pistons and valves move to and fro in straight lines, and do not tend to automatically place themselves in such positions as to trap the oil properly and keep the surfaces from touching. Neither can the large extent of surface exposed be kept flooded with oil, the passage of live steam through the valve-chest and cylinders not admitting the presence of large quantities of oil. We have therefore to be content with the presence of a lubricating film of no great thickness, and either make the loads on the bearing surfaces small or cause them to move somewhat slowly.

For a proper understanding of the conditions under which the efficient lubrication of steam-valves and cylinders takes place, it is necessary to consider at some length the physical properties both of the lubricant and of the steam.

Evaporation of Oil.—Even at ordinary temperatures water, when in a dry atmosphere, evaporates, the vapour mixing with the air and making it moist. Such evaporation goes on until the air is saturated with moisture. Somewhat similar conditions occur at the free surface of a mineral oil. Such oils slowly evaporate until their vapours saturate the air or steam in contact with them. With ordinary bearings at ordinary temperatures there is very little loss by evaporation, when oil of good quality is used, but at the high temperatures of steam cylinders serious loss may occur, for not only is the tendency to evaporate increased, but the oil vapour is rapidly carried off with the great volume of steam passing through the exhaust. On this account mineral cylinder oils should be carefully tested as directed on p. 183, and all that are unduly volatile rejected.

Decomposition of Lubricants.—Vegetable and animal oils are unsuitable for cylinder lubrication, as, in contact with steam, at the high temperatures to which they are subjected, they undergo a chemical change resulting in the formation of free fatty acids (p. 100) which may give rise to very serious corrosion. In many instances, the use of such fatty lubricants has resulted in the cylinder metal being rendered quite spongy and porous in the course of a few years: bolts, valve-spindles, studs, and other parts have been cut quite through, and cylinder joints, etc., rendered leaky.

The steam passages also become choked with metallic soaps, oxides of iron, and free carbon, resulting from the chemical action of the fatty acids upon the cylinder metal, and the destructive decomposition effected by heat and high-pressure steam. In locomotives the oil thrown against the hot blast-pipe, and even that adhering to the ports, undergoes destructive distillation with formation of a carbonaceous deposit, which accumulates and gradually blocks up the passages. A partial analysis of such a deposit scraped from a piston head is given below.

Fixed carbon,	35·37
Hydrocarbons soluble in ether,	7·52
Neutral fatty oil,	3·07
Fatty acids, free, and combined with metallic oxides,	2·52
Ash: chiefly oxides of iron, with small quantities of copper oxide, lead oxide, etc.,	44·85
Moisture,	2·21
Undetermined and loss,	4·46
	100·00

Fatty oils, however, when mixed with mineral oils, in quantities not exceeding 5 to 20 per cent., do not seem to produce these objectionable results so readily: indeed, the lubrication of parts which have to carry very heavy loads is greatly improved by the addition of such oils.

When surface condensers are used, and the condensed water is again passed into the boilers, great care must be exercised to prevent the passage of the oil used for the lubrication of the cylinders into them. Tallow, suet, castor oil, and other animal and vegetable lubricants must not be used in such cases, even in small quantities, for the acids liberated by the action of heat and water vapour pass into the boilers and cause serious corrosion. These acids cannot be separated from the water by merely allowing it to rest for a time in a tank: they remain to a large extent suspended in the water, giving it a translucent appearance. Mineral oil also remains in condensed water in a very fine state of division, and even though a considerable quantity may rise to the surface and be removed, sufficient remains in suspension to produce very serious effects upon the flues. Indeed, its presence may so check the passage of heat through the plates as to cause them to collapse. When the water is passed through a coke filter before entering the boiler, and thereby made bright and clear, no corrosive action appears to take place, the grease, etc., being for all practical purposes eliminated.

The deleterious effects produced by the action of a lubricant on marine boilers, when surface condensers have to be used, have led to marine engines being run without any lubrication whatever of their steam-chests or cylinders. This can often be done without any very serious wear taking place, for the load on the rubbing surfaces of many well-designed engines is very small, but with new engines slow speeds must be adopted to begin with, and the surfaces allowed to 'burnish' and acquire hard skins.

Application of Cylinder and Valve Lubricants.—Even when the lubricant used for cylinders is a good one, it is sometimes found that the parts are improperly lubricated. This may arise from several causes, most of which, however, can be traced to superficial tension phenomena.

It has already been explained that water will not touch the oiled surface of a solid, although the comparative superficial tensions of metal, oil, and water are such that the latter has a greater affinity for the metal than oil has. But oil cannot be readily moved from a metallic surface by water, for the oil is nearly insoluble, and evaporates very slowly. On the other hand, water may be readily replaced by oil, owing to the facility with which the water evaporates and leaves a comparatively clean surface for the oil to cover. The superior affinity of a metallic surface for water rather than oil is also shewn by the rapidity with which water will displace the oil from a bearing where there is abrasion going on, and will cause it to run hot. The presence of water in a steam-cylinder or steam-chest is consequently deleterious. The friction of the faces rubs off the oil, and if water be present in bulk, it covers the surfaces, and if the loads be heavy, they grind and tear in the absence of a lubricant.

The condensation which takes place in a long steam-pipe will often send so much water into the engine cylinders that lubrication becomes impossible. To prevent this, separators are fitted so as to dry the steam before it is used. A vertical exhaust pipe not fitted with a drain pipe to carry away the water will also cause wear and tear of the valves, for the water condensed in the cylinders cannot get away freely. Difficulty is often experienced when valves are placed on the top of the cylinders, for the water in the cylinders and steam-chest cannot escape, but remains on the cylinder bottom and the valve faces.

The D valves of non-compound high-pressure engines, especially when not balanced, press very heavily upon their faces, but the stroke being small, and the speed of rubbing low, the heating effect is not large. The pressure upon them, however, is so great, that where at their ends there is any considerable length of valve seating which, owing to the short stroke, is not exposed to the steam, the surfaces are apt to grind and tear. To ensure the proper lubrication of this part of the valve face, grooves may be cut in it, as shown in fig. 122.

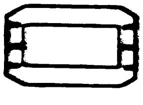


FIG. 122.

We have in a previous chapter described one or two forms of lubricator designed to steadily introduce a lubricant into the steam space without entailing loss of either steam or oil. Such a lubricator is generally placed above the point where the steam-pipe enters the steam-chest. It must not be placed above the main steam-valve, for when the engine is not at work, the steam-pipe may become filled with condensed water and the lubricator allowed to feed into it. Rising up the water-logged steam-pipe, the oil will flow into the boiler, and may cause serious injury there. The pipe conveying the oil from the lubricator should be carried well into the steam-pipe, so that the lubricant may be delivered into the rapid current of steam and not allowed to run down the sides of the pipe. Indeed it is a good plan to carry the oil supply pipe right across the steam-pipe, and allow the oil to escape through a number of side perforations. When this is done, the oil escapes at several points, is well distributed over the column of steam in the steam-pipe, covers the surface of each particle of water passing with the steam, or is carried as spray to all parts of the steam-chest. The water particles, being covered with a pellicle of oil, then lubricate instead of merely wetting with water the surfaces upon which they impinge.

Lubrication of Cutting Tools.—The cutting edge of a tool, such as that used for a lathe, drill, slotting, or other machine, is, owing to its hardness, enabled to imbed itself in the softer metal. When the metal is being worked, especially if it be a tough one, heat is developed, not only owing to the friction against the tool, but also owing to the distortion suffered by the strip cut off. A large proportion of the heat developed distributes itself in the mass of metal, while some of it spreads to the tool, raising its temperature and occasionally seriously injuring its temper. To prevent this, a stream of liquid is directed against the tool. Water is generally used, but owing to the rapidity with which plain water rusts clean iron surfaces, it has to be mixed with soap of some kind, which also acts as a lubricant.

At the cutting point there is actual metallic contact, and the friction is mainly that of an unlubricated surface, *i.e.*, the friction decreases with increasing speeds of cutting. The increase of speed consequently decreases the load on a drill, although the heat produced may be somewhat greater. On this account it is well, should a drill break, to first try a higher rather than a lower speed, unless the heating effect produced be already too high to admit of such a change.

In many shops the speeds of machines are lower than they need be, for it is sometimes assumed that breakages can only be prevented by running at low speeds. Mineral oils, being deficient in oiliness, are not suitable for high-speed tools which require good lubrication. Fatty oils, such as lard oil, or a mixture of soft soap and soda, from 14 to 16 lbs.

of each to 100 gallons of water, are greatly superior. The water, having a high specific heat, keeps the tools cool, whilst the soap and soda improve its lubricating qualities as well as prevent the surfaces from rusting (see p. 125).

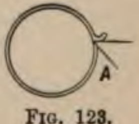


FIG. 123.

The exact effects produced by a lubricant upon the working of a cutting tool, at least so far as driving power is concerned, are not clearly understood. That the lubricant penetrates to the neighbourhood of the cutting edge is shewn by the increased smoothness of the finished surface, and by the greater force required to keep the tool against the work. The lubricant finds its way almost, if not quite, to the cutting edge through the gap at A (fig. 123). The edge of the tool, being lubricated best on the side A nearest the work, is unable to dig in and tear the metal, which is therefore finished smooth and partially burnished. All bearings should be finished with a very sharp and well lubricated tool, no emery being used if the metal be at all soft.

Frictional Losses.—*Magnitude of Losses.*—The losses which arise from the friction of the mechanism, as compared with the total energy actually expended in useful work, are in many cases unduly large. As an extreme case, a clock or watch may be instanced. Here, practically, the whole of the power is expended in overcoming the friction of the bearings, and the efficiency is zero. Should the friction of the pinions increase or diminish from any cause, then that of the speed-regulating appliance likewise diminishes or increases, the total friction remaining constant.

In a cotton mill, woollen factory, or printing works, the frictional losses are very large compared with the power actually developed. Here we have to deal with losses in the motor, the transmission machinery, and also in the actual machine tool, the power expended in placing the threads in position, or propelling the paper, ink rollers, etc., being small. In electric light and hydraulic stations the efficiency of the installation is greater, for the total power delivered in the form of current, or volume of water raised, is large in comparison with that developed by the motors.

Ordinary atmospheric changes of temperature have at times been known to alter the friction of the machinery of a large mill as much as 15 or 20 per cent. In other instances a reduction of 50 per cent. in the total resistance, and, therefore, of the fuel, etc., used, has been effected by using a more suitable oil. When it is remembered that this means that the frictional loss sometimes amounts to considerably more than half the power developed by the motor, the importance of using a suitable lubricant will be fully appreciated.

As the viscosity decreases, sometimes rapidly, with rise of temperature, a lubricant which may be suitable for one season or country may not suit another. The effects brought about in this way may be seen by comparing the coal burned from week to week during the year with the changes the mean temperature has undergone during the same intervals. In railway work this is particularly noticeable, the coal consumption, partly on this account, being much greater during winter months than in the summer.

Even after a mill has stood for a day, the bearings will have cooled down so much that considerably more power will be required to work it during the first few hours than during the rest of the run, providing the temperature of the air does not fall much in the interval. This must be borne in mind when, for the purpose of ascertaining the efficiency of any particular lubricant, the indicated horse-power required to drive a mill is measured.

The Efficiency of Mechanism.—In a machine shop or factory where power is used for carrying on any process, we generally have a *prime mover* which renders available the energy derived from some natural source, and *transmission machinery* for conveying the power so obtained to any point for the actuation of *special machinery* or *machine tools*. The mechanical efficiency of the motor or of any link in the mechanism involved in the transmission of power is obtained by dividing the useful work performed by the gross energy expended. Thus in the case of a steam engine, if the indicated horse-power be 100, and the work actually delivered on the belt be 85, the efficiency would be ·85.

In some cases the losses arising from the friction of shafting, etc., are so great that it is more economical to transmit the power electrically from the prime mover to the machine, which is then fitted with a small electric motor.

Electrical Transmission of Power.—The use of electrical methods for the transmission of energy is now engaging the serious attention of mechanical engineers, for it enables the frictional losses of bearings to be to a large extent avoided. The resistance of the electrical conductors, however, also results in considerable loss of energy, and their capital cost being also large, electrical methods of transmission are not always the most economical; but where power has to be transmitted to a number of scattered points, it is often best to have a well-designed central generating station and to transmit the energy electrically to the several shops or yards.

Economical Lubrication.—Before one can establish the fact that a particular oil is more economical in use than another, a balance sheet must be drawn up showing the total expenses chargeable to each of the following items:—

1. Cost of power developed.
2. Cost of proportion of power lost in friction.
3. Expenses resulting from wear and tear.
4. Cost of lubricants.

When the lubricants are very unsuitable, the bearings improperly designed, or there is careless management, other losses may be incurred which will not fall under either of the above heads. They include broken shafts, heated bearings, rapid wear, etc. It is such signs that often first direct attention to the fact that the lubricants in use are unsuitable. Even when such accidents are comparatively rare, the loss by friction may be much greater than it ought to be, and the fact that comparatively little difficulty is experienced in keeping the bearings from actually getting hot should not be regarded as shewing that good results are being obtained as regards economy of power.

Indicating of Motors.—When once the necessary gear has been fitted for indicating an engine, the difficulty of ascertaining the horse-power at any given moment is very small. Apart from the question of friction, a large motor should have indicator diagrams taken periodically for the purpose of ascertaining whether the valves are properly set and the distribution of steam satisfactory. For the best method of procedure, a work on the indicator should be consulted. We may here point out, however, that fluctuations in speed and power are produced by the action of the governors, etc., from minute to minute, and that accurate figures can only be obtained by making a series of observations extending over a reasonable interval of time, the mean of the results obtained from each set of indicator cards being made use of.

Estimation of Cost of Frictional Losses.—As in many cases almost the whole of the losses are due to the friction of lubricated bearings, the losses due to each portion of the mechanism should, as far as possible, be ascertained separately. This may be done by obtaining the indicated horse power under the following conditions:—

(*a*) Motor running light.

(*b*) With the transmission machinery in motion.

(*c*) With all the machines, or certain types of machines, running light.

(*d*) With all the machines, or certain types of machines, having their full working load on.

As the viscosity of lubricants varies with the temperature, the tests to ascertain the comparative lubricating value of two oils, etc., should be made under similar atmospheric conditions, and it is of equal, if not of greater, importance to give the bearings time to assume a steady temperature by indicating the motor at the end of a few hours' run.

To obtain the actual cost per hour per horse-power developed in ordinary running, the calculation should include the following items:—

1. Interest on cost of land, plant, and buildings.
2. Depreciation (maintenance and renewal).
3. Taxes, insurance, etc.
4. Wages and salaries.
5. Cost of fuel, oil, waste, etc.

Here we have a number of charges which increase or decrease the cost of power according as the mean output decreases or increases. It may be argued that the saving effected by improving the lubrication, inasmuch as it does not decrease some of these items, should be calculated upon the saving in item 5 only. However, when the saving in power is large, it may affect depreciation and wages as well. This is a point the consideration of which must be left to the judgment of the engineer in charge.

It has been shewn that the friction of a steam-engine or gas-engine is unaffected by the load put upon it. Thus if, when running light, the indicated horse-power is 7, then when the brake horse-power is 50, the indicated horse-power will be 57. From this it is clear that the frictional resistance, measured when there is no load on the engine, gives the frictional resistance under all conditions. The same will apply to line shafting and to many machines and machine tools. We may therefore estimate very closely the friction-reducing properties of any particular lubricant by running the machinery oiled with it light, rather than fully loaded; care must, however, be taken always to have the same number of machines at work when making a test.

When the horse-power developed by the motor is large, and the machines numerous, the effect of changing an oil can only be ascertained by using it on a large number of bearings or machines, so as to make the loss or gain of power considerable in proportion to, the total effect.

By multiplying the gain or loss of power by the cost per horse-power, and then by the hours worked per diem, the daily saving or loss is obtained, and by comparing this with the oil account the real commercial value of the lubricant is ascertained. This point has been dealt with at some length by R. H. Thurston.[*]

Since the increase in friction of a bearing results in a rise of the temperature of the pedestal, a rough idea of the comparative value of two lubricants may be obtained by measuring their temperature effects. This is most satisfactorily effected by surrounding two bearings on a shaft by roomy boxes, to protect them from draughts, and placing thermometers in contact with the pedestal caps. The same oil should first be tried on both bearings, and the rise of temperature of each noted, for with the same oil different bearings will almost always be found to give somewhat different heating results. When the difference of temperature which results from the accidental difference of load or condition of each bearing has been ascertained, the oil used for one of them may be changed and a comparative test again made. This should be done several times, for the result depends in some measure upon the rate of feed.

It is, however, much more satisfactory to make such oil-tests in proper oil-testing machines, for the load, speed, and rate of and method of feed, can then be properly controlled.

Estimation of Losses due to Wear.—These can only be obtained in a direct way by comparing the expense incurred in repairs, renewals, and breakdowns, which have occurred during fairly long intervals of time. However, it is sometimes necessary to obtain the effects produced during short intervals by different lubricants, in which case the best plan is to weigh certain brasses or other rubbing parts, such as piston rings, at stated intervals on an accurate balance. In this way any rapid increase or decrease in the rate of wear can be noted, and this, taken in connection with the pecuniary gain or loss resulting from a variation in the total frictional losses, will enable the engineer to form a fairly accurate estimate of the value, from a practical point of view, of any particular lubricant.

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[*] *Oil and Colourman's* Journal, 1st October 1894. Friction *and Lost Work* (*Third Edition*), p. 343.

In all cases where frictional losses form a large proportion of the power developed, it will be found that the cost of the lubricant, being only about 3 per cent. of the cost of fuel, is a comparatively insignificant item compared with that of the power saved or lost. Indeed, it will frequently pay to use the best lubricant irrespective of its price. The highest-priced lubricant offered, however, is often by no means the best, for very poor mixtures are sometimes placed upon the market as first-class lubricants and sold at high prices.

Oil-cans, Feeders, etc.—Vessels for holding a supply of oil and enabling it to be supplied to the bearings with ease and certainty are made of various patterns. In some cases it is only necessary to supply a few drops once every few hours. For this purpose small conical or lenticular cans, having a long spout screwed on, are convenient. Either the bottom or sides are made elastic, and a little pressure exerted compresses them and expels a small quantity of oil. In the larger forms the oil is liberated by opening a small valve actuated by a button, or the piston of a small cylinder is pressed in and any desired amount of oil delivered.

It sometimes happens that the reservoirs of oil-bath bearings have to be emptied and filled again periodically. For this purpose a form of syringe is used which enables a definite quantity to be withdrawn from the bottom of the reservoir and fresh oil substituted.

THE END.

INDEX.

Abel test for flashing-point, 179.
Acetone test for rosin oil in mineral oil, 284.
Acetyl value, determination and meaning of, 235–240.
—— —— determination, necessity of precautions to prevent oxidation, 239.
—— —— determination of, by Benedikt's method, 236.
—— —— determination of, by Lewkowitsch's method, 238.
—— —— of oils (*Benedikt*), table of, 237, 238, 240.
—— —— of oils (*Lewkowitsch*), table of, 239, 240.
—— —— of oxidized oils, 239.
Acetyl acid value, determination and meaning of, 236.
Acetylation of mixed wax alcohols, use of, and method, 231–233.
Acid, free, or acidity of oils (section on), 201–209.
—— —— amount permissible in lubricants, 208, 209, 300.
—— —— determination of, 206–208.
—— —— effects of, in lubricants, 204–206, 395.
—— —— effect of storage on, 204.
—— —— gravimetric estimation of, 208.
—— —— methods of expressing, 206, 207.
—— —— nature and amount of, in fixed oils, 201–204.
—— —— nature and amount of, in mineral oils, 201.
Acid value, meaning of, 206.
Adamson (Daniel); force-pump lubrication, 362.
Adhesion; Tait on, 3.
Agate for bearings, 354.
Aisinmann; determination of flashing-point, 181.
Allbright and Clark; cloth-oil tester, 269.
Alcohols, wax, acetylation process of examination, 231–233.
—— —— acetylation process, results obtained by (*table*), 234.
—— —— from beeswax, properties and identification of, 221, 224, 233, 234.
—— —— from carnauba wax, 221, 224, 233, 234.
—— —— from sperm oil, 221, 224, 233, 234.
—— —— from wool fat, 221, 224, 233, 234.
—— —— iodine values of, 246.
—— —— specific gravities of, at $\frac{100^\circ}{100^\circ}$ C., 177.
Alén; arachidic acid in rape oil, 105.
Alkali value, meaning of, 214.
Allen; free acid in oils, effect of, 206.
—— lard oil, properties of, 312.
—— Milliau test for cottonseed oil, 279.
—— Reichert values of oils, 231, 232.
—— 'saponification equivalent' of oils, 214.
—— sperm oil, flashing-point of, 315.
—— tallow; water, blood, and insoluble matter in, 310.
—— tallow oil, specific gravity of, 311.
Almond oil, comparative oxidizability of, 256.
Aluminium for bearings, 353.
Amagat and Jean; differential refractometer, 198.
Amalgamation produced by pressure, 3.
American mineral oils (see *Mineral lubricating oils*).
Amontons; friction research, 6.
Analysis of greases, 317.
—— of mixed lubricating oils, 214, 317.
'Animal oil;' acid free, in, 202, 311.
—— —— acetyl value of, 239.

iodine value of, 311.
Maumené thermal value of, 252.
aponification value of, 311.
etting-point of, 311.
pecific gravity of, 311.
see also *Tallow oil*).
, distinction of from vegetable 222.
see *Fixed oils*).
rthnut) oil, acetyl value of, 237.
etection and estimation of, in oil, 273.
dine value of, 244, 245.
dine value of mixed fatty from, 245.
aumené thermal value of, 252.
elting- and solidifying- point ixed fatty acids from, 197.
idation, increase of weight 57, 259.
idizability of, 256.
fractometer value of, 199.
eichert-Meissl value of, 232.
ponification value of, 213.
tting-point of, 191.
ecific gravity of, 176.
ecific gravity of mixed fatty from, 177.
saponifiable matter in, 223.
id, free, in oils, 202, 203, 204,

atty, chemical action of, on 205.
l oil,' properties of, 311.
oil, estimation of, in olive oil, 274, 275.
ils, acetyl values of, 240.
e thermal test, 248.
il, solubility of, in alcohol, 308.
, properties of, 312.
né thermal test, 250.
test for cottonseed oil, 279.
oils, ash of, 292.
cid test for cottonseed oil, 277.
l, characters of, 202, 306.
l, arachidic acid in, 105, 276.
e mineral acid in, 301.
ponification value of, 304.
sting for cottonseed oil in, 304.
t-Meissl values of oils, 231.
point, determination of, 188.
ickened oils, analysis of, 121.
iodine value of, 310.
ty of oils, 184.
eter, 184.
ricant for bearings, 354.
for heavy loads, 409.
nation of, 292.
ion found in mineral lubri- g oils, 292.

Ashcroft, oil-testing machine (*drum*), 330.
Asphalt, detection and estimation of, in mineral oils, 288–290.
'Astatki,' characteristics of, 93.
—— difference from American 'residuum,' 93.
—— fractional distillates from, (*table*), 96.
—— manufacture of lubricating oils from, 93, 95.
Axle-box bearings, 373.
—— for grease, 375.
—— for oil, 373–375.
—— heating of locomotive, 418.
—— locomotive, 374.
—— railway vehicle, 374.

BABBIT'S metal for bearings, 351.
Bach; method of determining melting-point, 195.
—— oxygen-absorption test, 260.
Badouin; colour reaction for sesamé oil, 280.
'Bagasses' oil, 106, 108.
Bailey's oil-testing machine (*pendulum*), 340.
Ball-bearings, design of, 383.
Ballantyne; acid, free, in oils, 203, 204.
—— acidity of oils, effect of storage on, 204.
—— rancidity of oils, 204.
—— (see *Thomson*).
Baynes (see *Fox*).
'Bayonne' engine oil, viscosity of, 159, 161.
Beal; estimation of volatile fatty acids, 229.
Beam (see *Leffmann*).
Bearings, adjustable brasses for, 373.
—— alloys for (*table* xciv.), 349.
—— aluminium, 353.
—— axle-box, 373.
—— ball, 383.
—— —— friction of, 83.
—— —— frictional laws of, 84.
—— —— purposes used for, 83.
—— bronze, 347–349.
—— burnished, 344.
—— bush, 369.
—— carrying power of, dependent upon viscosity of lubricant, 363.
—— case-hardened, 344.
—— cast-iron, 347.
—— chilled cast-iron, 344.
—— collar, lubrication of, 380.
—— conditions determining area of and load on, 365.
—— —— determining form of, 366.
—— corrosion of, by free fatty acids, 204–206.

ngs, cylindrical, effects of load on wear of, 81.
—— forms of, 369–379.
design and lubrication of, 341–392.
—— estimation of surface hardness of, 345.
—— exposed, hard materials required for, 343.
fit of, 366.
flexibility of, 368.
forms of, 341.
grinding of hard, 344.
gun-metal, 347.
—— heating, cause of, 14.
—— high-speed, 373.
—— jewelled, for watches, 370.
—— loads admissible on, 364, 367.
—— —— on locomotive, 374.
loose fit of, necessary, 367.
materials for, 342.
netals for low speed, 56.
tals, selection of, for, 5.
ture of opposing surfaces of, 341.
n-metallic materials for, 354.
erheating of, 416.
edestal, 370.
— with side pads, 371.
ot, 381.
e surface, 379–382.
—— positions for oilways of, 359–361.
—— protecting greases and japans for, 416.
—— protection of, from dust, 342.
—— pump circulation for, 373.
—— railway vehicle, treatment of heated, 413.
—— regular examination of, 414.
—— reservoir, with disc oil-lifters, 372.
—— —— with oil-lifting chains, 371.
—— —— with oil strainers, 373.
—— —— with ring oil-lifters, 372.
—— roller, 384.
—— —— purposes used for, 85.
—— rolling contact, 382–384.
—— spindle, Parsons', 375.
—— steel, hard, 343.
—— subject to alternating pressures, 81.
—— variable load, 377.
—— watch and clock, 369.
—— wear of well-lubricated, 368.
—— white-metal, action of acids on, 350.
—— white-metals for, 349–353.
—— woods for, 353.
—— workmanship, importance of good, 368.
Becchi; test for cottonseed oil, 278.
Beechnut oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-point of mixed fatty acids from, 245.
Beechnut oil, oxidation, increase of weight by, 257.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
Beechwood for bearings, 353.
Beeswax, hydrocarbons in, 233.
—— estimation of hydrocarbons in, 235.
—— iodine value of, 245.
—— melting-point of, 196.
—— saponification value of, 213.
—— specific gravity of, 176.
—— sp. gr. of unsaponifiable matter from, 177.
—— unsaponifiable matter from, characteristics of, 221, 224, 233, 234.
—— —— determination of, 218.
—— —— percentage of, 223.
Bender; asphalt in mineral lubricating oil, 288.
Benedikt; 'acid value' of oils, 206.
—— (and Ulzer), acetyl values of oils (*table*), 237.
—— —— determination of acetyl value, 236.
Bensemann; method of determining melting-points of fats, 195.
Benzoline, from petroleum naphtha, 90.
Berthelot; cohesion of water molecules, 33.
Bevan; Becchi's reaction given by oxidized lard, 279.
—— melting-point of fat reduced by chilling, 192.
Bishop; method of determining oxidizing property of oils, 258.
Bitumen destructively distilled yields oil, 89.
Black (see *Evans* and *Black*).
Blackfish oil (see *Dolphin oil*).
Black Sea rape oil (see *Ravison oil*).
Blending of lubricants, 399.
Bloede; factitious viscosity of mineral oils, 121.
Bloom (see *Fluorescence*).
Bloomless oil, manufacture of, 93.
Blown oils, acetyl values of, 237, 240.
—— —— as lubricants, 118, 119.
—— —— characteristics of, 117.
—— —— chemical changes caused by blowing, 117, 118.
—— —— detection and identification of, 315, 316.
—— —— distinction between cottonseed and rape, 316.
—— —— estimation of, in mixed oils, 225.
—— —— Hehner values of, 228.
—— —— iodine values of, 246.
—— —— manufacture of, 117.

Blown oils, miscibility of, with mineral lubricating oils, 117.
—— —— Reichert-Meissl values of, 232.
—— —— relation between sp. gr., iodine value and saponification value of, 316.
—— —— saponification values of, 213.
—— —— solubility of, in alcohol and petroleum spirit, 117.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed fatty acids from, 177.
Bochin; railway train friction, 9.
Boiler fittings, lubricants for, 409.
Boilers, exclusion of lubricants from, 410, 420.
Boiling-point of mineral lubricating oils, 97.
Bone-fat, ash in, 292, 311.
—— free fatty acid in, 311.
—— iodine value of, 245.
—— iodine value of mixed fatty acids from, 245.
—— lime in, 292.
—— melting-point of, 196.
—— melting- and solidifying-point of mixed fatty acids from, 197.
—— saponification value of, 213.
—— specific gravity of, 176.
Bone oil, absorption of oxygen by, 261.
—— —— as lubricant for clocks and watches, 311.
—— —— comparative oxidizability of, 256.
Bottlenose oil (see *Sperm oil*).
Box-wood for bearings, 353.
Boys (Vernon); properties of soap-films, 32.
Brazil-nut oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
Bromine thermal test, 247–250.
—— —— value, relation of to Hübl iodine value, 248–250.
Bruyn and Van Leent; refractometer values of oils, 199.
Buckley's piston-rod bearing, 380.
Buisine; process for estimating hydrocarbons in beeswax, 235.
Burning-point of oils, 178.
Burstyn; effects of free acid in lubricants, 204.

CAMELINE oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— refractometer value of, 199.
—— —— saponification value of, 213.
Cameline oil, setting-point of, 191.
—— —— specific gravity of, 176.
Canewood for bearings, 353.
Caoutchouc in mineral oils, 290.
Capillarity, 42–44.
Capillary force, (see *Superficial Tension*), 31–48.
—— tube, energy of flow in, 27.
—— —— flow through, 22.
—— —— inlet end resistance of, 28.
—— —— rise of liquids in, 45.
Carboid for bearings, 354.
Carnauba wax, iodine value of, 245.
—— —— melting-point of, 196.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed alcohols from, 177.
—— —— unsaponifiable matter from, characteristics of, 221, 224, 233, 234.
—— —— unsaponifiable matter from, percentage of, 223.
Carpenter (Lant); railway wagon grease, 123.
Cart-grease from Galician petroleum, 86.
Castor oil, acetyl value of, 237–240, 308.
—— —— acid, free in, 203.
—— —— characteristics of, general, 109.
—— —— cold, effect of, on, 109.
—— —— composition of, 109.
—— —— constants of genuine, 302.
—— —— expression of, from the seed, methods of, 109.
—— —— Hehner value of, 309.
—— —— iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— lubricant for low speeds, 405.
—— —— lubricant for railways in India, 101.
—— —— Maumené value of, 252, 309.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidizability of, comparative, 256.
—— —— refining, methods of, 109.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— Reichert and Meissl values of, 232, 309.
—— —— saponification value of, 213, 309.
—— —— setting-point of, 191.
—— —— solubility of, in alcohol, 308.
—— —— solubility of, in mineral oil, 109.
—— —— solubility of mineral oil in, 109, 110.
—— —— source of, 108.
—— —— specific gravity of, 176, 308.

Caster oil, testing of, systematic, 308–309.
— — unsaponifiable matter, percentage of, in, 223.
— — viscosity of, 159, 161, 308.
Cerasin, melting-point of, 196.
— saponification value of, 213.
— specific gravity of, 176.
Caryl acetate, yield and saponification value of, 234.
Cetyl acetate, yield and saponification value of, 234.
Cetyl alcohol in spermaceti, 233.
Chattaway; refractometer value of sperm oil, 199.
Chemical testing of lubricants, 295–318.
Chlorophyll in vegetable oils, 99.
Cholesterol acetate, yield and saponification value of, 234.
— characteristics of, 222.
— colour reactions of, 281, 282.
— distinction of, from isocholesterol, 223.
— — and separation from phytosterol, 222.
— iodine value of, 246.
— occurrence of, in wool fat, liver oils, etc., 215, 219, 222, 233.
Clague; melting-point of cacao butter modified by heating, 192.
Clay-slate for bearings, 354.
Clayton; friction of railway vehicles, 63.
— railway wagon grease as lubricant, 124.
Cloth-oil testers, 269, 270.
Coal-tar oil, specific gravity of, 177.
Coconut oil, acid, free, proportion of, in, 111.
— — characters, general, of, 110.
— — constants of, 303.
— — expression and extraction, methods of, 110.
— — iodine value of, 245, 309.
— — iodine value of mixed fatty acids from, 245.
— — lubricant for light machinery, use as, 101.
— — melting-point of, 196.
— — melting- and solidifying-points of mixed fatty acids from, 197.
— — Reichert and Meissl values of, 232, 309.
— — saponification value of, 213, 309.
— — source of, 110.
— — specific gravity of, 176.
— — testing of, 309.
Cod-liver oil, iodine value of, 245.
— — melting- and solidifying-points of mixed fatty acids from, 197.
— — oxidizability of, comparative, 256.
Cod-liver oil, refractive index of, 198.
— — refractometer value of, 199.
— — Reichert and Meissl values of, 232.
— — saponification value of, 213.
— — setting-point of, 191.
— — specific gravity of, 176.
— — unsaponifiable matter, percentage of, in, 223.
Cohesion between copper surfaces, 3.
— — glass surfaces, 3.
— — lead surfaces, 3.
— — marble surfaces, 3.
— figures, 44.
— pressure and, 5.
— Tait on, 3.
Cold-test (see *Setting-point*).
Coleman; spontaneous combustion of oily waste, 268.
— viscometer, 140–143.
Coleseed (rapeseed), 102.
Collar bearings, lubrication of, 380.
Colophony (rosin), destructive distillation of, 119.
— — detection of, in oil, fat, or grease, 284.
— — estimation of, by Twitchell's process, 227–229.
— — iodine value of, 246.
— — specific gravity of, 176.
Colour reactions of cholesterol, 281, 282.
— — of cottonseed oil, 277–280.
— — of phytosterol, 281–282.
— — resin acids, 284–288.
— — rosin oil, 282–284.
— — sesamé oil, 280, 281.
Colza (seed, oil), 102.
Connecting-rod oil cups, 378.
Consistence of fats and greases, determination of, 162–164.
Contamination films, 5.
— liquid surface, 40.
— solid surface, 36.
Cook; method of determining melting-point, 195.
Corn oil (see *Maize oil*).
Corrosion of metals by free fatty acids in oils, 204–206.
— of steam cylinders by fatty acids, 100.
Coste and Parry; properties of commercial neatsfoot oil, 313.
Cottonseed oil, acetyl value of, 237–239.
— — acid free, in, 202.
— — blown, acetyl value of, 240.
— — blown, distinction of, from blown rape oil, 316.
— — blown, Hehner value of, 228.
— — blown, iodine value of, 246.

tonseed oil, blown, Reichert-Meissl value of, 232.
— —— colour reactions of, 277, 278, 280, 304.
— —— iodine value of, 244, 245.
— —— iodine value of mixed fatty acids from, 245.
— —— Maumené value of, 252.
— —— melting- and solidifying-points of mixed fatty acids from, 197.
— —— oxidation, increase of weight of, by, 257, 259.
— —— oxidizability of, comparative, 256.
— —— oxygen, absorption of, by, 260, 261.
— —— refractive index of, 198.
— —— refractometer value of, 199.
— —— Reichert and Meissl values of, 232.
— —— saponification value of, 213.
— —— setting-point of, 191.
— —— specific gravity of, 176.
— —— specific gravity of mixed fatty acids from, 177.
— —— unsaponifiable matter in, percentage of, 223.
ttonseed stearin, iodine value of, 245.
— —— iodine value of mixed fatty acids from, 245.
— —— melting-point of, 196.
— —— melting- and solidifying-points of mixed fatty acids from, 197.
— —— saponification value of, 213.
— —— specific gravity of, 176.
ulomb; friction research, 6.
— laws of solid friction, 7.
— on flow through capillary tubes, 23.
cking of mineral oil (see also *Destructive Distillation*), 91.
nk-pin, lubrication of, 359.
ton oil, acetyl value of, 237.
— —— Reichert-Meissl value of, 232.
cas oil, acetyl value of, 239.
— —— iodine value of, 245.
— —— melting- and solidifying-points of mixed fatty acids from, 197.
— —— Reichert-Meissl value of, 232.
— —— saponification value of, 213.
— —— setting-point of, 191.
— —— specific gravity of, 176.
inder oil from astatki, 96.
— —— 'valvoline,' 159, 161.
inder oils, filtered, manufacture of, 92.
— —— flashing-points of, 178.
— —— (mineral), viscosity of, 159, 161.
— —— oxygen, absorption of, by, 261.
— —— reduced, manufacture of, 92.
— —— viscosity of, 298.
— —— volatility of, 183–186.
Cylinders and valves, application of lubricants to steam-, 421.
—— —— imperfect nature of lubrication of steam-, 419.
Cylinders, steam-, lubricators for, 385–391.
—— —— corrosion of, by fatty acids, 100, 420.
—— —— design of, 391.
—— —— drain valve for, 391.
—— —— passages, deposits in, 420.
—— —— water, effect of, in steam-, 36, 421.
Cylindrical bearings, effects of load and speed on pressure-film of, 73.
—— —— results produced by wear of, 72.

DALICAN'S 'titre test,' 196, 311.
Deeley; lubricator for steam-cylinders, 389.
—— and Wolff, lubrication of plane parallel surfaces, 64.
Deering; free acid in tallow, castor oil, and sperm oil, 203.
—— (and Redwood), solubility of castor oil in alcohol, 308.
—— —— viscosity of castor oil, 308.
Deggut or 'goudron,' from Russian petroleum, 95.
De Negri and Fabris; estimation of arachis oil in olive oil, 275, 276.
—— —— iodine value of olive oil, 306.
Density, determination of, 172.
—— of lubricating oils, effect of change of temperature on, 173, 175.
—— of water at 4° to 100° C., 174.
—— relation of, to specific gravity, 164.
—— (see also *Specific Gravity*).
Deprez and Napoli's oil-testing machine (*disc*), 338.
Destructive distillation, 89, 90.
Diffusion of metals, 4.
Distillation, destructive, 89, 90.
—— *in vacuo*, 92, 93.
Distilled oils, manufacture of, from astatki, 95, 96.
—— —— manufacture of, from residuum, 92–95.
—— —— manufacture of, from shale, 96.
Dolphin-body oil, Hehner value of, 228.
—— —— iodine value of, 245.
—— —— Reichert value of, 232.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
Dolphin-jaw oil, composition of, 115.
—— —— constants of, 116, 303.
—— —— Hehner value of, 228.
—— —— identification of, 315.
—— —— iodine value of, 245.
—— —— lubricant for watches, 115, 408.
—— —— preparation of, 115.
—— —— Reichert value of, 232.

Dolphin-jaw oil, saponification value of, 213.
Donath; chemical action of fatty acids on metals, 205.
ng liquids, composition of, 125.
r; retarded ebullition, 38.
—; molecular adhesion, 17.
—— superficial solubility, 40.

nut oil (see *Arachis*).
ny of lubricants, 410.
al transmission of power, 424.
grease-box, 375.
ood for bearings, 353.
ions, nature of, 42.
magnitude of surface, 41.
il from astafiki, 96.
, viscosity of, 159, 298.
—— asphalt in mineral oil, 286.
ssion of viscosity, 145
kler viscometer, 145–147.
dard viscometer, 144–145.
determination of iodine value,
4.
Black); estimation of resin acids
Twitchell's process, 228, 229.
n of oil in steam cylinders, 419.
ntinuity of static and kinetic coefficients of friction, 57.
—— friction and speed, 8.
Examinations, bearing, book for record of, 415.

Fats, consistence, determination of, 162–164.
—— iodine value of (*table*), 225.
—— melting- and solidifying-points, determination of, 193–198.
—— melting-points of (*table*), 196.
—— melting of, phenomena observed in the, 192.
—— saponification values of (*table*), 213.
—— specific gravities of, at 60° F. (*table*), 176.
—— unsaponifiable matter in, percentage of (*table*), 223.
Fatty acids, acetylation of, by Benedikt's method, 236.
—— —— action of acetic anhydride on, 235, 237, 238.
—— —— chemical action of, on metals, 204–206.
—— —— free, in oils (see *Acid*).
—— —— free, in oils, determination of, 206–208.
—— —— free, in oils, gravimetric estimation of, 208.
—— —— free, permissible amount of, in lubricants, 208, 209.
—— —— insoluble, estimation of, 226.
Fatty acids, insoluble, estimation of, in presence of hydrocarbons and wax alcohols, 227.
—— —— insoluble, preparation of, 228.
—— —— melting- and solidifying-points, determination of, 192–198.
—— —— melting of, phenomena observed in the, 192.
—— —— mixed, of oils, iodine values of (*table*), 245.
—— —— mixed, of oils, melting- and solidifying-points of (*table*), 197.
—— —— mixed, of oils, specific gravities of, at $\frac{100^\circ}{100^\circ}$ C. (*table*), 177.
—— —— mixed, of oils (see also under individual oils).
—— —— occurring in lubricating oils, (*table*), 102.
—— —— preparation and properties of, 191.
—— —— volatile, estimation of, 229.
Fatty oils (see *Fixed oils*).
Fenton's metal for bearings, 351.
Films, contamination, 5.
—— heating of lubricating, 363.
—— liquid, stability of, 38.
—— —— tension of, 31.
—— lubricating, critical velocity in, 24.
—— —— effect of heat on, 39.
—— —— plastic flow in, 30.
—— —— strength of, 54.
—— —— thickness of, 357.
—— —— viscous flow in, 67.
—— oiliness of lubricating, 37.
—— oily or greasy lubricating, 31.
—— plastic lubricating, 29.
—— pressure-, effect of load on thickness of, 364.
—— pressure-, friction of, 358.
—— properties of, Reinold on, 38.
—— —— Rücker on, 38.
—— solubility of superficial, 40.
Film-test for oxidizing and gumming properties of oils, 255.
—— —— by Holde with various fixed oils, 256.
Filters, oil, 401, 403.
Finkener; test for rosin oil in mineral oil, 285.
—— test for purity of castor oil, 308.
Fire caused by spontaneous ignition of oily rags, etc., 268.
Firing-point ('fire-test'), determination of, 178.
Fish oil, comparative oxidizability of, 256.
Fixed oils, acetyl values of (*tables*), 237–239.
—— —— acid, free, in, nature and amount of, 201.

Fixed oils, chemical action of, on metals, 204–206.
—— —— decomposition of, in steam-cylinders, 100.
—— —— detection of, in mineral oils, 209.
—— —— detection of mineral oils in, 210.
—— —— differences from mineral oils, 99–101.
—— —— drying, semi-drying and non-drying, 99, 100.
—— —— estimation and identification of, in mixed oils, 224–226.
—— —— flashing-points of, 178.
—— —— Hehner values of (*table*), 228.
—— —— iodine values of (*tables*), 244, 245.
—— —— Maumené values of (*table*), 252.
—— —— oxidation and gumming of (see *Oxidation*), 254–261.
—— —— oxygen in, percentage of, 99.
—— —— properties of, 99.
—— —— refining small quantities of, process for, 209.
—— —— Reichert and Meissl values of (*table*), 232.
—— —— saponification values of (*table*), 213.
—— —— setting-points of, 187.
—— —— sources and composition of, 99.
—— —— specific gravities of, at 60° F., 99, 164, 176.
—— —— unsaponifiable matter in, percentages of (*table*), 223.
Flashing-point, Abel test for determining, 179.
—— 'closed test' for, 179.
—— determination of, 179–183.
—— Gray's tester for determining, 181.
—— limits of safety, 178.
—— meaning of, 178.
—— of cylinder oils, 178.
—— of fixed oils, 178.
—— of mineral lubricating oils, 97, 178.
—— 'open test' for, 179.
—— Pensky-Martens test for, 179.
—— volatility of oils compared with, 186.
Fluorescence, or 'bloom,' 93, 97.
—— characteristic of hydrocarbon oils, 220.
—— destroyed by nitronaphthalene, etc., 292.
—— how best seen, 220.
Fox; chemical action of fatty acids on lead, 204, 205.
—— oxygen absorption test, 260.
—— (and Baynes), changes caused by blowing oils, 117.
—— (and Baynes), Hehner values of blown oils, 228.
Fractional distillation, 90.
Freezing of lubricants, 396.
Freezing-point (see *Setting-point*).
Friction, brake, 10.
—— coefficient of, 6.
—— coefficient of, at low speeds with good lubrication, 57.
—— coefficient of, between metals, 8.
—— coefficient of, with varying loads and speeds, 61.
—— cohesion and, 3.
—— contamination films and, 5, 7.
—— continuity of static and kinetic coefficient of, 57.
—— cylindrical bearing, 74, 75.
—— due to viscosity of pressure-film, 358.
—— effects of area and load upon, 81.
—— effects of area upon cylindrical bearing, 79.
—— effects of method of lubrication and contact area upon, 82.
—— effects of speed on dry, 8, 10.
—— effects of viscosity on, of cylindrical bearings, 76.
—— effects, on machinery at low speeds, 56.
—— estimation of losses due to, 425.
—— Goodman on losses from, 51.
—— heating by, 14.
—— high speed, due to viscosity of lubricant, 355.
—— influence of viscosity of lubricant on, 56.
—— kinetic coefficient of, 6.
—— laws of solid, 10.
—— leather belt, 9.
—— liquid (see *Viscosity*), 16–29.
—— losses resulting from, with lubricated bearings, 51, 423.
—— of machines, 1.
—— 'Magnolia' metal, Smith's experiments on, 8.
—— Morin's apparatus, 6.
—— pivot, variation of, with speed and load, 69.
—— plastic lubricating film, 52.
—— plastic, nature of, 29.
—— Rennie's experiments on, 7.
—— rolling, 2, 3, 13.
—— rope, 1.
—— seizing, produced by, 5.
—— sliding, 2.
—— solid, 1, 2, 7.
—— solid, nature of, 2.
—— static coefficient of, 6.
—— static coefficient of lubricated surface, 52.
—— static, viscosity and, 52.
—— surface condition, influence of, on, 7.
—— theory of solid, by Hele Shaw, 9.
—— thin lubricating film, 51.
—— variation of, with speed, 354.

n, wear l by, 3.
n-clutches, wear of, 2.
ol test for sesamé oil, 281.
ss lubricator, 391.

ON (Douglas); brake friction experiments, 11.
ne, 99.
tin' for thickening mineral oils, 120, 291.
ly; spontaneous ignition of oily waste, 268.
' oil, viscosity of, 159.
in, determination of specific gravity of, 166.
rol and water, determination of viscosities of, 130–134.
—— viscosities of at 20° C. (*table*), 134–137.
ann; estimation of volatile fatty acids, 229.
n; change of coefficient of friction with increasing load and speed, 61.
efficient of friction at low speeds, 57.
sses resulting from bearing friction, 51.
w speed friction, experiments on, 58, 60.
ickness of oil films, 357.
— iscosity and cylindrical bearing friction, on, 78.
Goodman's mechanical testing machine (*drum*), 334.
'Goudron,' characteristics of, 95.
—— lubricating grease made from, 95.
Grapeseed oil, acetyl value of, 237.
Graphite for heavy loads, 405, 409.
Gray; flashing-point apparatus, 181.
Grease, analysis of, systematic, 317.
—— cart, from Galician petroleum, 86.
—— consistence of, methods of measuring the, 162–164.
—— 'cup,' manufacture of, 122.
—— detection of soap in, 291.
—— detection of inorganic substances and starch in, 291.
—— 'engine,' manufacture of, 122.
—— melting of, phenomena observed in the, 192.
—— melting-point, determination of, 192–198.
—— quantity consumed in railway wagon lubrication, 124.
—— railway wagon, 123.
—— rosin, manufacture of, analyses, and uses of, 124, 125, 405.
—— soap-thickened, manufacture and analyses of, 121–124.
Grease-cup lubricator, 385.
Greasiness, property of lubricants, 31, 396.
Gripper; approximate analysis of mixed lubricating oils, 214.
Gumming of oils sometimes due to free acids, 206.
—— and oxidation of lubricating oils, 254–267, 395.
—— (see also *Oxidation*).
Gun-metal for bearings, 347.
Gypsum for bearings, 354.

HADDOCK-LIVER oil, iodine value of, 245.
—— —— specific gravity of, 176.
Hagenbach on estimation of energy of capillary flow, 27.
Hall, Proctor; measurement of surface tension, 46–48.
Halphen; colour reaction of cottonseed oil, 280.
Hardness, measurement of, 345.
Heat, mechanical equivalent of, 14.
Heating of bearings, 416.
—— viscosity and, 417.
Hedge-mustard oil, 103.
Hedge-radish oil, 103.
Hefford, C. E.; on crank-pin lubrication, 359.
Hehner; observation on Beechi's cottonseed oil test, 279.
—— (and Mitchell), bromine thermal test, 247, 248.
Hehner value, determination of the, 226.
—— —— of fixed and blown oils (*table*), 228.
—— —— use of in the analysis of lubricants, 226.
Hele-Shaw; theory of solid friction, 9.
Hempseed oil, acetyl value of, 237.
—— —— iodine value of, 245.
—— —— of mixed fatty acids from, 245.
—— —— oxidation of, change of weight by, 259.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— refractometer value of, 199.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— unsaponifiable matter, percentage of, in, 223.
Hesse; colour test for cholesterol, 281.
Hickory (wood) for bearings, 353.
Hide for wheel teeth, 354.
High speeds, viscosity of oils for, 298.
Hirn; friction of lubricated surfaces, 9.
Hofmeister; methods for determination of setting-points, 189.
Holde; asphalt and resin in mineral oils, 288–290.
—— changes undergone by mineral oils exposed to air in thin films, 261–267.

Holde; colour reaction of rosin oil, 283.
—— detection of fatty oil in mineral oil, 210, 315.
—— detection of mineral oil in fatty oil, 210.
—— detection of nitronaphthalene, 292.
—— detection of water in oils, 292.
—— determination of flashing-point, 180–181.
—— Engler's viscometer, use of, 145.
—— organic acids in mineral oils, 209.
—— oxidation of fixed oils, 256.
—— oxygen absorption test, 260.
—— paraffin in mineral oils, estimation of, 287.
—— Reichert-Meissl values of oils, 231.
Holly (wood) for bearings, 353.
Holt; drain valve for steam cylinders, 391.
Hooper; acidity of commercial neatsfoot oil, 313.
Horse fat, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting-point of, 196.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— Reichert and Meissl values of, 232.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
Horse foot oil, acetyl value of, 239.
Howat, A.; drop sight-feed lubricator, 385.
Hübl iodine process, chemical reactions of the, 240, 241, 243–247.
—— —— value (see *Iodine Value*).
'Huile tournante' ('huile d'enfer'), 107.
Hurst; volatility of machine oils, 183.
Hydrocarbon oils (see *Mineral lubricating oils*, *Rosin oil*).
Hydrocarbons, identification of, in unsaponifiable matter, 219.
—— occurrence of, in beeswax, 233.
Hydrolysis of fatty esters, 100.
Hydrometers, 169–171.

Illuminating oils from petroleum, 87, 90.
—— —— yield increased by cracking, 91.
Ingham and Stapfer; oil-testing machine (*drum*), 330.
Iodine value calculated from bromine thermal test, 248–250.
—— —— calculated from Maumené test, 254.
—— —— comparative results by Hübl and Wijs's processes, 244.
—— —— determination of, by Hübl's process, 241–244.
—— —— determination of, by Wijs's process, 244.
Iodine value, meaning and use of, in analysis of oils, 240.
—— —— of blown oils, alcohols, resins, solid hydrocarbons, mineral lubricating oils, and rosin oil (*table*), 246.
—— —— of fixed oils, fats and waxes (*table*), 245.
—— —— of mixed fatty acids (*table*), 245.
Isocholesterol, characteristics of, 222.
—— distinction of, from cholesterol, 223.
—— occurrence of, in wool fat, 222, 223.

Jacoby's alloy for bearings, 351.
Japan wax, iodine value of, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
Jean (Amagat and), differential refractometer, 198.
—— —— refractometer values of oils, 199.
Jenkin; continuity of static and kinetic coefficient of friction, 8, 57.
Jenkins; bromine thermal test, 248.
Jessop; lubrication of connecting-rod big-ends, 378.
Jewelled bearings, 370.
Joule; mechanical equivalent of heat, 14.
Journals, corrosion of, by free fatty acids in oils, 204.

Kelley's watch oil, results of examination of, 116.
Kelvin; law of molecular attractions, 33.
—— liquids for illustrating interfacial tension, 34.
—— superficial solubility, 40.
Kerosene illuminating oil from petroleum, 90.
Kimball on friction and speed, 8.
—— on low speed friction, 57, 60.
Kingston's metal for bearings, 351.
Kissling; apparatus for determining consistence of fats, 162.
—— oxidation of linseed oil, 257.
—— spontaneous heating of oily fibrous mineral, 268.
Koettstorfer; 'degrees' (of acidity), 206.
—— value (saponification value), 210–214.
Kunkler; apparatus for determining consistence of fats, 162.
—— viscometer, 145–147.

Laplace; stability of liquids and solids in contact, 36.
'Lapping' (process of grinding hard metals), 3.

Lard, iodine value of, 245.
—— iodine value of mixed fatty acids from, 245.
—— lubricant, with graphite, for heavy loads, 405.
—— melting-point of, 196.
—— melting- and solidifying-points of mixed fatty acids from, 197.
—— Reichert-Meissl value of, 232.
—— saponification value of, 213.
—— specific gravity of, 176.
—— unsaponifiable matter, percentage of, in, 223.
Lard oil, characters, general, and composition of, 113.
—— —— coefficient of friction (static) with, 52.
—— —— congealing point of, in relation to iodine value, 312.
—— —— constants of genuine, 303.
—— —— iodine value of, 245, 312.
—— —— Maumené value of, 312.
—— —— preparation of, from lard, 112.
—— —— refractometer value of, 199.
—— —— saponification value of, 213, 312.
—— —— setting-point of, 191.
—— —— specific gravity of, 176, 312.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— testing for adulterants in, 312.
—— —— unsaponifiable matter, percentage of, in, 312.
Leeds; resin acids in rosin oil, 124.
Leffmann and Beam; use of glycerol for Reichert-Meissl process, 230.
Leonard; detection of nitronaphthalene, 282.
Lewis, W. T.; watch and clock bearings, [illegible].
Lewkowitsch; acetyl value, determination of the, 237, 238.
—— acetyl values of oils (table), 239.
—— acetyl values, relation to Benedikt's values, 239.
—— acid, free, in palm oil, 292.
—— cholesterol, action of potash-lime on, 235.
—— colophony, estimation of, by Twitchell's process, 229.
—— iodine value, determination of the, 244.
—— Millian test for cottonseed oil, 279.
—— neatsfoot oil, properties of, 313.
—— nitric acid test for cottonseed oil, 277, 278.
—— rosin oil, specific gravity of, 119.
—— sperm oil, alcohols of, 233.
—— sperm oil, composition of, 114.
—— tallow, iodine value of, 310.
Lewkowitsch; unsaponifiable matter, relation of, to fire risk, 269.
Liebermann; colour reaction of cholesterol, resin acids and rosin oil, 282-284.
Lignum vitæ for bearings, 353.
Limestone for bearings, 354.
Linseed oil, acetyl value of, 237, 239.
—— —— blown, Hehner value of, 228.
—— —— iodine value of, 244.
—— —— iodine value of mixed fatty acids from, 244, 245.
—— —— Maumené value of, 252.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidation of, increase of weight by, 257, 259.
—— —— oxygen, absorption of, by, 260.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— Reichert-Meissl value of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— unsaponifiable matter, percentage of, in, 223.
Liquids, miscibility of, 34.
Livache; drying of oils by oxidation, 254.
—— test for oxidation of oils, 256, 257.
Loads admissible on bearings, 367.
—— on ball bearings, 383.
—— on pivot bearings, 382.
—— on plane surface bearings, 379.
Lobry de Bruyn; detection of mineral oil in sperm oil, 210, 315.
Locomotive engines, loads on bearings of, 374.
—— —— lubrication of bearings of, 374.
—— —— viscosity of oils for, 298.
Lovibond's tintometer for observing the colour of oils, 297.
Lubricants, acidity of, 395.
—— adulteration of, 393.
—— age, changes produced by, 400.
—— analysis by expert advisable, 394.
—— blending of, 399.
—— boiler fitting, 409.
—— clarification of, 401.
—— cost and efficiency of, 410.
—— decomposition of, 420.
—— filters for, 401.
—— freezing of, 396.
—— friction of solid, 6.
—— genuineness of, 393.
—— greasiness of, 396.
—— grit, etc., in, 404.
—— gumming of, 395.
—— high speed, 407.

Lubricants, kinds of, suitable for various loads and speeds, 399, 405–410.
—— low-speed, 405.
—— measurement of efficiency of, 418.
—— mechanical testing of, 319–340.
—— methods of applying, 384.
—— miscellaneous machine, 407, 408.
—— mixed fatty and mineral oils, 54.
—— —— analysis of, 317, 318.
—— moderate speed, 406.
—— nut and bolt, 409.
—— oiliness of, 396.
—— plumbago, for cast-iron, 347.
—— precipitation of paraffin wax in, 400.
—— selection of, 410.
—— solid, 409.
—— solid, shear of, 5.
—— staining by, 398.
—— straining of, 398, 404.
—— testing of, by physical and chemical methods, 295–318, 394.
—— testing of, by mechanical methods, 319–340.
—— use of fats and greases as, 401.
—— variable oiliness of, 39.
—— viscosity of, 397.
Lubricating films, effect of heat on, 39.
—— —— formation of, 64.
—— —— formation of cylindrical-bearing, 73.
—— —— formation of plane parallel, 65.
—— —— thickness of cylindrical bearing, 76.
—— —— thin, at low speeds, 55, 62.
Lubricating oils, composition and identification of unsaponifiable matter in, 219–224.
—— —— containing sperm oil or wool fat and mineral oil, analysis of, 233.
—— —— density, alteration in, caused by change of temperature, 173, 175.
—— —— expansion of (see alteration in density), 173, 175.
—— —— mineral (see *Mineral lubricating oils*).
—— —— mineral, proportion of, obtained from crude petroleum, 87.
—— —— mineral, spoiled by destructive distillation, 91.
—— —— mixed, approximate analysis of, 214.
—— —— mixed, estimation and identification of the saponifiable oil in, 224–226.
—— —— mixed, estimation of unsaponifiable matter in, 215–219.
—— —— mixed, systematic analysis of, 317.
Lubricating oils, oxidation and gumming of, 254–267.
—— —— oxygen, absorption of, by, 260, 261.
Lubrication, abrasion, importance of, to prevent, 55.
—— bath-, 83.
—— bath-, Tower's experiments on, 362.
—— collar bearing, 380.
—— conditions of, 51.
—— connecting-rod big-end, 378.
—— contamination films and, 49.
—— cutting tools, of, 422.
—— cylinder, effects of water on, 54, 421.
—— economical, 424.
—— effects of film-strength on, 54.
—— efficiency of, at different loads and speeds, 61.
—— efficient, 384.
—— equations illustrating conditions of pivot, 68.
—— force pump, 362.
—— friction reduced by, 49.
—— greases used for low speed, 63.
—— heating of lubricating films, 363.
—— high speed pressure-film, 64.
—— imperfect, 82.
—— low speed, 50.
—— —— conditions of, 55.
—— means of effecting, 2.
—— methodical habits of, 413.
—— objects of, 49.
—— oil-pump distribution, 385.
—— oil-spray chambers, 358.
—— oily pad, 83.
—— pad, Tower's experiments on, 361.
—— plane parallel surface, conditions of, 64.
—— 'perfect,' 50.
—— —— advantages of, 356.
—— plastic solids, use of, for, 63.
—— saturated pad, 83.
—— static, 51.
—— steam cylinder and valve, 419–422.
—— superficial solubility and, 40.
—— theory of, 49–84.
—— —— high speed, 50.
—— —— low speed, 62.
—— —— the lubrication of cylindrical surfaces, 72–81.
—— —— the lubrication of inclined plane surfaces, 69–72.
—— —— the lubrication of plane parallel surfaces, 65.
—— viscous flow and, 17.
Lubricator, Deeley, for steam cylinders, 389.
—— displacement, for steam cylinders, 387.
—— drop sight-feed, 385

Lubricator, Furness, for steam cylinders, 391.
—— grease cup, 385.
—— Ottewell, for steam cylinders, 388.
—— Roscoe, for steam cylinders, 387.
—— siphon, 385.
Lungwitz (see *Schweitzer*).
Lux's test for fatty oil in mineral oil, 209.

MACHINERY, cleanliness of, 411.
—— efficiency of, 411.
—— heavy, viscosity of oil for, 298.
—— high speed, viscosity of oil for, 298.
—— light, viscosity of oil for, 298.
—— lightness and efficiency of modern, 412.
—— management of, 411–418.
—— miscellaneous, lubrication of, 407.
—— oil, dark medium, viscosity of, 159, 161.
—— —— light, from astatki, 96.
—— oil-testing (see *Testing machines*), 319–340.
—— preservation of standing, 415.
—— starting new, 412.
M'Ilhiney; estimation of rosin oil in mineral oil, 286.
Mackey; cloth-oil tester, 270, 271.
—— —— results obtained with, 271.
—— spontaneous ignition of oily materials, 268, 269.
—— unsaponifiable matter, relation of to fire-risk, 269.
MacNaught's testing machine (*disc*), 336.
Magnolia metal for bearings, 351.
—— —— mechanical test of, 352.
Maize oil, acetyl value of, 239.
—— —— iodine value of, 244, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— Reichert value of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— unsuitability of, for lubrication, 101.
—— —— unsaponifiable matter, percentage of, in, 223.
Manganese bronze for bearings, 348.
Maple (wood) for bearings, 353.
Marangoni; behaviour of liquids in contact, 34.
—— stability of liquids and solids in contact, 36.
Marine-engine cylinders sometimes not lubricated, 421.
Marine engines, viscosity of oil for, 298.
Maumené thermal test for oils, 250–252.
—— thermal values of oils (*table*), 252.
—— thermal value, relation of, to iodine value, 254.
Maxwell on viscous and plastic flow, 29.
Mayer (L.); examination of tallow for cottonseed oil or stearin, 310.
'Mazut,' residuum from Russian petroleum, 93.
Mechanical testing of lubricants, 319–340.
Mechanism, efficiency of, 424.
Meissl (see *Reichert*).
'Melon oil' from head of dolphin, 115.
Melting-point, determination of, preparation of substance for, 193.
—— —— by Bach's method, 195.
—— —— by Bensemann's method, 195.
—— —— by capillary tube method, 194.
—— —— by Cook's method, 195.
—— —— by Pohl's method, 193.
—— —— by Stock's method, 193.
—— of fats and greases, 192–198.
—— of lubricants, objects of determining, 192.
Menhaden oil, iodine value of, 245.
—— —— Maumené value of, 252.
—— —— Reichert value of, 232.
—— —— specific gravity of, 176.
—— —— unsaponifiable matter, percentage of, in, 223.
Metals, corrosion of, by fatty acids in oils, 204–206.
—— diffusion of, 4.
—— relative hardness of, 345.
Michelson; on measurement of superficial tension, 46.
Milliau test for cottonseed oil, 278.
—— test for sesamé oil, 281.
Mineral acid, free, determination of, in oils, 208.
—— —— in refined rape oil, 301.
—— —— permissible amount of, 209.
Mineral lubricating oils, acid, free, in, 201, 209, 299.
—— —— ash in, proportion and estimation of, 292, 299.
—— —— asphalt in, detection and estimation of, 288–290, 300.
—— —— boiling-point of, 97.
—— —— caoutchouc, detection of, in, 290, 300.
—— —— cold-test of, 97.
—— —— colour of, 296.
—— —— composition of, 97, 98.
—— —— detection of, in fatty oil, 210.
—— —— fatty oil, detection of, in, 209, 299.
—— —— fire-risk of, 269.
—— —— flashing-point of, 97, 178, 297.
—— —— grit and dirt in, 300, 404.

Mineral lubricating oils, gumming of, 261–267, 300, 395.
—— —— inorganic substances, detection of, in, 291.
—— —— iodine value of, 98, 246.
—— —— manufacture of, 89–97.
—— —— odour of, 296.
—— —— oxygen, absorption of, by, 261.
—— —— paraffin, estimation of, in, 287.
—— —— properties and composition of, 39, 97–99.
—— —— purposes suitable for, 407.
—— —— refractive index of, 198.
—— —— rosin oil in, detection and estimation of, 284–286, 299.
—— —— saponifiable oil, estimation of, in, 219.
—— —— saponification value of (*nil*), 213.
—— —— setting-point of, 97, 187, 192, 298.
—— —— soap, detection of, in, 291, 299.
—— —— sources of, 86–89.
—— —— specific gravity of, 97, 177, 297.
—— —— spontaneous combustion prevented by, 269.
—— —— systematic testing of, by physical and chemical methods, 296–300.
—— —— viscosity, determination of, 297.
—— —— viscosity of, 159, 160, 161.
—— —— viscosity of, factitious, 120, 121.
—— —— volatility of, 183–186, 297, 419.
—— —— volatility and flashing-point of, compared, 186.
Miscibility, interfacial tension and, 35.
Mitchell (see *Hehner*).
'Mixing-oils' prepared from solar oil, 95.
Molecular stresses, intensity of, 33.
Molecules, liquid attractions of, 32.
—— stresses on surface, 33.
Moore; constants of porpoise and dolphin jaw oils, 116.
—— Reichert values of oils, 231, 232.
Morawski; colour reaction of resin acids, 284.
Morin; frictional research, 6.
Motors, indication of, 425.
Mustard oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidizability of, comparative, 256.
—— —— refractive index of, 198.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.

Myricyl acetate, yield and saponification value of, 234.
—— alcohol, occurrence of, in beeswax and carnauba wax, 233.

NAPHTHA, crude, from petroleum, 90.
Napier on friction and viscosity, 363.
'Natural oils,' 92.
Neatsfoot oil, acid, free in, 312.
—— —— characters, general, of, 113, 312.
—— —— cold effect of, in, 113.
—— —— constants of genuine, 303.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— preparation of, 113, 312.
—— —— purposes suitable for, as lubricant, 101, 113, 406, 408.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— testing of, for adulterants, 312, 313.
—— —— unsaponifiable matter in, per cent., 313.
—— —— used as lubricant for clocks, 113.
—— —— used for mixing with mineral oil, 101.
'Neutral oil,' manufacture of, 93.
Niger-seed oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— Maumené thermal value of, 252.
—— —— refractometer value of, 199.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
Nitrobenzene and nitronaphthalene, detection of, 292.
Nitronaphthalene, used for destroying fluorescence or 'bloom,' 93.
Nordlinger; free acid in castor oil, 203.
Nuts, lubricant for, 409.

OAK (wood) for bearings, 353.
Octadecyl acetate, yield and saponification value of, 234.
—— alcohol in spermaceti, 233.
Oil-cups, cleaning and examination of, 415.
Oil-feeders, 427.
'Oil-pulp' or 'thickener,' 120, 291.
Oil stains, 398.
Oil-testing machines (see *Testing machines, mechanical*), 398.

Oil-ways in locomotive bearings, 374.
—— —— positions for, 359–361.
Oiliness, important property of lubricants, 31, 38, 39, 396.
Oils, animal and vegetable (see *Fixed oils*).
—— blown (see *Blown oils*).
—— fatty (see *Fixed oils*).
—— fixed (see *Fixed oils*).
—— lubricating (see *Lubricating oils*).
—— mineral lubricating (see *Mineral lubricating oils*).
—— mixed (see *Lubricating oils*).
—— undescribed, systematic testing of, 295.
ve oil, acetyl value of, 237–239.
—— —— acid, free, in, 202, 305.
—— —— arachis oil in, detection and estimation of, 273, 306.
—— —— as lubricant, 101, 405, 408.
—— —— chemical composition of, 108.
—— —— chlorophyll in, 306.
—— —— constants of genuine, 302.
—— —— copper in, detection of, 305.
—— —— extraction of, from olives, 106.
—— —— furfurol reaction given by, 281.
—— —— iodine value of, 244, 245, 306.
—— —— iodine value of mixed fatty acids from, 245.
—— —— Maumené value of, 252, 307.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidation, increase of weight of, by, 257, 259.
—— —— oxidisability of, comparative, 256.
—— —— oxygen, absorption of, by, 260, 261.
—— —— refining of, 108, 305.
—— —— refractive index of, 198.
—— —— refractometer value of, 199, 305.
—— —— Reichert-Meissl value of, 232.
—— —— saponification value of, 213, 306.
—— —— setting-point of, 191.
—— —— source of, 106.
—— —— specific gravity of, 176, 306.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— testing of, systematic, 305–307.
—— —— unsaponifiable matter in, per cent., 223, 307.
—— —— varieties of ('virgin,' 'superfine,' etc.), 106.
—— —— viscosity of, 159.
Olive-kernel oil, characters of, 108.
—— —— iodine value of, 245.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
Ordway; cloth-oil tester, 269.
—— flashing-points of mineral lubricating oils, 178.
Ottewell; lubricator for steam cylinders, 388.
Ox oil, oil from beef tallow, 311.
Oxidation and gumming of lubricating oils, 254–267, 395.
—— accelerated by finely divided metals, 257.
—— Bishop's test, 258.
—— film-test, 255.
—— increase of weight of oils by, 256–258.
—— Livache's test, 256.
—— of mineral oils, 261–267.
—— products of, 257.
—— watch-glass test, 255.
Oxidized oils, acetyl values of, 239.
Oxygen absorption test for gumming properties of oils, 260, 261.
Ozokerit, iodine value of, 246.
—— (see also *Ceresin*).

Packing, metallic, for piston rods, 382.
Pads, examination of lubricating, 415.
'Pale' (mineral) oils, 92, 97.
Palm oil, acid, free, in, 110, 202, 309.
—— —— characters of, 110.
—— —— composition of, 110.
—— —— constants of genuine, 302.
—— —— extraction, method of, 110.
—— —— iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting-point of, 196.
—— —— melting-point of mixed fatty acids from, 197.
—— —— Reichert and Meissl values of, 232.
—— —— saponification value of, 213.
—— —— source of, 110.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— testing of, 309.
—— —— unsaponifiable matter in, per cent., 223.
—— —— used for making railway wagon grease, 101.
Palm-nut oil, characters and composition of, 110.
—— —— distinction of, from other fats, 309.
—— —— Hehner value of, 228.
—— —— iodine value of, 245, 309.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting-point of, 196.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— Reichert and Meissl values of, 232, 309.

m-nut oil, saponification value of, 213, 309.
— —— source of, 110.
— —— specific gravity of, 176.
raffin oils,' 92.
affin wax, estimation of, in mineral lubricating oils, 287.
— —— identification of, in unsaponifiable matter, 220.
— —— iodine value of, 246.
— —— manufacture of, from petroleum and shale oil, 90, 96.
— —— melting-point of, 196.
— —— saponification value of (*nil*), 213.
— —— specific gravity of, 176, 220.
ry (see *Coste*).
sons, Hon. C. A.; spindle-bearing, 375.
sons' metal for bearings, 351.
ch-kernel oil, acetyl value of, 237.
rmain; refractometer values of oils, 199.
lestal bearings, 370, 373.
sky-Martens flashing-point apparatus, 179–181.
tecost; on removal of oil-stains from abrics, 399.
roleum, crude, characters and composition of, from various countries, 87–89.
— —— estimated annual production of, 87.
— —— nature and occurrence of, 86.
— —— percentage of illuminating and lubricating oil in, 87.
— —— products obtained from, 90.
osphor-bronze for bearings, 348.
ytosterol, characteristics of, 222.
— colour reactions of, 281.
— distinction and separation of, from cholesterol, 222.
— iodine value of, 246.
— occurrence of, in vegetable oils, 215, 219, 222.
s, lubrication of, 379.
ton-rod, metallic packing for, 352, 382.
— non-metallic packing for, 64.
ots, theory of lubrication of, 64, 69.
stic friction, 29, 52.
ckles (Agnes); contamination of liquid surfaces, 40.
iseuille's formula for flow of liquid through capillary tubes, 23, 127.
larimetric test for rosin oil in mineral oil, 285.
nzio; arachidic acid in rape oil, 105, 276.
ppyseed oil, acetyl value of, 237.
— —— iodine value of, 245.
— —— iodine value of mixed fatty acids from, 245.
Poppyseed oil, Maumené value of, 252.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidation of, increase of weight by, 257, 259.
—— —— oxidizability of, comparative, 256.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— Reichert-Meissl value of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— unsaponifiable matter in, per cent., 223.
Porpoise-body oil, Hehner value of, 228.
—— —— iodine value of, 245.
—— —— Reichert-Meissl values of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
Porpoise-jaw oil, chemical constants of, 116, 303.
—— —— composition of, 115.
—— —— extraction of, from head-fat of porpoise, 115.
—— —— Hehner value of, 228.
—— —— identification of, 215.
—— —— iodine value of, 245.
—— —— Reichert and Meissl values of, 232.
—— —— saponification value of, 213.
—— —— source of, 115.
—— —— used for lubricating watches, etc., 101, 115, 408.
Power, cost of producing, 424.
Pressure-film (lubricating), conditions under which formed, 64.
—— —— form of, on cylindrical bearings, 73.
—— —— Tower's measurements of thickness of, 75.
Pulley, loose-, Smith's self-oiling, 376.
Pyknometer, instrument for taking specific gravity, 164.
'Pyrene oil' (decomposed refuse olive oil), 106, 108.

Ragosine, V. I.; commences manufacture of lubricating oils from astatki, 95.
Railway cars, viscosity of oil for, 298.
Rancidity of oils, not the same as acidity, 204.
Rape oil, acetyl value of, 237, 239.
—— —— acid, free, in, 105, 202, 301.
—— —— acid, free sulphuric, in, 105, 301.
—— —— arachidic acid in, 105.

Rape oil, Black Sea, see Ravison oil.
—— —— blown, acetyl value of, [illegible]
—— —— blown, preparation of, from blown [illegible], [illegible]
—— —— blown, Hehner value of, [illegible]
—— —— blown, iodine value of, [illegible]
—— —— blown, Reichert-Meissl value of, [illegible]
—— —— characteristics of [illegible], 218.
—— —— characteristics of Indian, 218.
—— —— [illegible] effect of, on, 215, [illegible]
—— —— chemical composition of, 216, [illegible]
—— —— [illegible] of gumming, [illegible]
—— —— extraction and expression of, from the seed, [illegible]
—— —— iodine value of, [illegible], 305.
—— —— iodine value of mixed fatty acids from, [illegible]
—— —— Maumené value of, [illegible], 304.
—— —— melting and solidifying-points of mixed fatty acids from, [illegible]
—— —— oxidation of, increase of weight by, [illegible]
—— —— [illegible] of, temperature, [illegible]
—— —— oxygen, absorption of, by, 280, 281.
—— —— refining of, by alkaline processes, [illegible]
—— —— [illegible]
—— —— [illegible]
—— [illegible]
—— [illegible]
—— —— [illegible]
—— [illegible]
—— [illegible]
—— [illegible]
—— [illegible]
—— [illegible]
—— [illegible] matter in, per [illegible]
—— —— [illegible]
Ravison [illegible]
Ravison [illegible]
—— —— [illegible] value [illegible]
—— —— characteristics of, [illegible]
—— —— iodine value of, 243.
—— —— iodine value of mixed fatty acids from, 243.
—— —— Maumené value of, 251.
—— —— melting and solidifying-points of mixed fatty acids from, 177.
—— —— refractometer value of, 198.
Ravison oil, saponification value of, 212.
—— —— source of, 106.
—— —— specific gravity of, 176.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— unsaponifiable matter in, per cent., 223.
Rayleigh; cohesive force of water molecules, 33.
—— contact of liquids with solids, 54.
—— contamination of liquid surfaces, 40.
—— law of interfacial tension, 34.
—— strength of liquid films, 54.
"Red" engine oil, viscosity of, 159, 161.
"Reduced" oils, characteristics of, 92.
—— —— process of manufacture, 92.
Redwood (Boverton); expression of viscosity, 140.
—— standard viscometer, 138–140.
—— (Deering and), free acid in castor oil, 303.
—— (Deering and), solubility of castor oil in alcohol, 308.
—— (Deering and), viscosity of castor oil, 308.
Redwood (I. J.): action of oils on metals, 304.
—— grease, manufacture of, 121, 122.
Refining small quantities of oil, process for, 279.
Refraction test for oils, 195–200.
Refractive indices of oils (table), 198.
Refractometer, differential, of Amagat and Jean, 198.
—— tests of oils (table), 199.
Reichert process, 229.
—— values of oils (table), 232.
Reichert-Meissl process, 230.
—— —— values of oils (table), 232.
Reimer and Will: acid of high melting-point in rape oil, 276.
Reinold and Rücker: thickness of liquid films, 45.
Renard: composition of rosin oil, 120.
—— estimation of arachis oil in olive oil, 271, 272, 276.
"Residuum," characteristics of, 93.
—— difference between American and Russian, [illegible]
—— manufacture of distilled oils from, [illegible]
—— nature and source of, 87, 90.
—— yield obtained by cracking, 93.
—— see also Astatki.
Resins, detection and estimation of, in mineral oils, 288–290.
—— see also Colophony.
Reynolds (Osborne): conditions determining steady viscous flow, 25, 127.
—— —— heating of lubricating films, 263.

Reynolds (Osborne), lubrication of inclined plane surfaces, 69.
—— —— physical and mechanical viscosity, 23.
—— —— theory of rolling friction, 13.
—— —— thickness of lubricating oil-films, 357.
—— —— viscosity and lubrication, 31.
—— —— viscous flow between approaching surfaces, 67.
—— —— viscous theory of lubrication, 50.
'Rhigolene,' volatile spirit from crude petroleum, 90.
Richards; on Ordway's cloth-oil tester, 269.
Richmond; development of the Reichert process, 230.
Ritsert; rancidity of oils, 204.
Roberts-Austen; on diffusion of metals, 4.
Roller-bearings, design of, 384.
Rolls, lubricant for, 93.
Roscoe; lubricator for steam cylinders, 384.
Rosin (see *Colophony*).
Rosin grease, 124, 125.
Rosin oil, anhydrides and esters in, 120.
—— —— characters, general, of, 119.
—— —— colour reactions of, 282–284.
—— —— composition of, 120.
—— —— detection and estimation of, in mineral oil, 284–286.
—— —— drying properties of, 120.
—— —— iodine value of, 246.
—— —— manufacture of, from rosin, 119.
—— —— manufacture of grease from, 120, 124.
—— —— oxygen, absorption of, by, 261.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— resin acids in, 120.
—— —— rotation of, 120, 285.
—— —— solubility of, in acetone and alcohol, 284, 285.
—— —— specific gravity of, 119, 177.
—— —— used for batching jute, 120.
Rubsen seed and oil, 102.
Rücker; on thickness of oil-films, 45.
Ruhemann, detection of fatty oil in mineral oil, 209.
Russian machine oils, viscosity of, 159–161.
—— oils (see *Mineral lubricating oils*).
—— residuum (see *Astatki*).

SALKOWSKI; colour reaction of cholesterol, 281.
—— observation on setting-point of cod-liver oil, 187.
Saponification, nature of, 100.
—— equivalent (*Allen*), 214.
—— value, determination of, 211.
—— —— meaning and use of, 210, 214.
Saponification value of oils, fats, and waxes (*table*), 213.
Sardine oil, iodine value of, 245.
—— —— saponification value of, 213.
—— —— specific gravity of, 176.
—— —— unsaponifiable matter in, per cent., 223.
Saybolt's viscometer, 143, 144.
Schiff; colour reaction of cholesterol, 282.
Schöttner; viscosity of glycerol, 134.
Schultz; method for determining the setting-points of oils, 190.
Schweitzer; factitious viscosity of mineral oils, 121.
Schweitzer and Lungwitz; characteristics of genuine lard oil, 312.
—— —— characteristics of refined whale oil, 313.
—— —— determination of the iodine value, 244.
—— —— test for soap in mineral oil, 291.
Scotch method of determining the setting-points of shale oils, 188.
Scotch oils (see *Shale oil; Mineral lubricating oil*).
Scott-Moncrieff; friction and viscosity, 363.
Screwing liquids (see *Drilling liquids*), 125.
Seal oil, blown, Hehner value of, 228.
—— —— iodine value of, 245.
—— —— Maumené value of, 252.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— refractometer value of, 199.
—— —— Reichert value of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
—— —— unsaponifiable matter in, per cent., 223.
Seizing of lead, tin, wrought iron, etc., 5.
Sesamé oil, acetyl value of, 237.
—— —— colour reaction of, 280, 281.
—— —— iodine value of, 244, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— Maumené value of, 252.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidation of, increase of weight by, 257, 259.
—— —— oxidizability of, comparative, 256.
—— —— refractive index of, 198.
—— —— refractometer value of, 199.
—— —— Reichert and Meissl values of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.

sesame oil, specific gravity of, 176.
Setting-point, determination of, by Archbutt's method, 188.
—— —— by Hofmeister's method, 189.
– —— by Schultz's method, 190.
– —— by Scotch method, 188.
— by Tagliabue's apparatus, 191.
fixed oils, 187, 191.
mineral lubricating oils, 97, 187, 192.
neaning of, 187.
precautions necessary in determining, 187.
– (see also *Solidifying-point*).
le, bituminous, characteristics of, 89.
– —— products of destructive distillaon of, 89.
characteristics and composition , 89.
—— products obtained from, 96.
—— (see *Mineral lubricating oil*).
-liver oil, acetyl value of, 239.
—— iodine value of, 245.
—— refractometer value of, 199.
—— —— saponification value of, 213.
—— specific gravity of, 176.
T.; plumbago as lubricant for cast-iron, 409.
rosthen,' varnish for protecting bearings, 416.
Siphon-feed, oil-lifting power of trimmings, 418.
—— -lubricator, 385.
Skate-liver oil, iodine value of, 245.
—— —— specific gravity of, 176.
Slide-blocks, loads on, 380.
Slides, theory of lubrication of, 69–72.
Smith (Angus); oxygen absorption test, 260.
—— (Ford), design of bearings by, 381.
—— (R. H.); magnolia metal, test of, 352.
Snakewood for bearings, 353.
Soap, detection of, in mineral oils and greases, 291.
—— preparation of, from fixed oils, 100.
—— (bubble) films, Boys on, 32.
—— —— solution for making, 32.
—— (see also *Soft soap*).
—— -thickened greases, manufacture and analysis of, 121–124, 317, 318.
—— —— oils, 120, 121, 317, 318.
Soapstone, lubricant for heavy loads, 405, 409.
Soft-soap, purposes suitable for as lubricant, 409.
'Solar oil,' 95.
Solid lubricants, 409.
Solids, friction of, 1–15.
—— superficial tension of, 35.
Solidifying-points of fatty acids, 193-198.
—— determined by Dalican's titre-test, 196.
—— —— by Pohl's method, 193.
Solubility, interfacial tension affected by, 39.
—— superficial, 40.
Specific gravity and density, 164–177.
—— —— determination of, by bottle, 165.
—— —— determination of, by hydrometers, 169–171.
—— —— determination of, by Sprengel tube, 166.
—— —— determination of, by Westphal balance, 167–169.
—— —— of coal-tar oils, 177.
—— —— of glycerin, determination of, 166.
—— —— of mineral lubricating oils, 97, 164, 177.
—— —— of mixed fatty acids at $\frac{100^\circ}{100^\circ}$C., 177.
—— —— of mixed wax alcohols at $\frac{100^\circ}{100^\circ}$C., 177.
—— —— of rosin oils, 177.
—— —— of vegetable and animal (fixed) oils, 99, 164, 176.
—— —— of waxes, 176.
—— —— reduction of, from one standard to another, 172.
—— —— reduction to the vacuum, 171.
—— —— relation to hydrometer degrees (*table*), 171.
—— —— (see also *Density*).
Specific temperature reaction, 253.
Sperm oils, acid, free, in, 114, 203, 204, 314.
—— —— Arctic and Southern, comparison of, 313, 314.
—— —— characters, general, of, 114.
—— —— composition of, 114.
—— —— constants of genuine, 303.
—— —— estimation of, in presence of mineral oil, 233.
—— —— extraction of, from the blubber, 114.
—— —— flashing-point of, 315.
—— —— identification of the unsaponifiable matter from, 221, 224, 315.
—— —— iodine value of, 245, 314.
—— —— iodine value of mixed fatty acids from, 245.
—— —— iodine value of unsaponifiable matter from, 246.
—— —— lubricants for light machinery and spindles, 101.

Sperm oils, lubricants, as, purposes suitable for, 406, 408.
—— —— Maumené value of, 314.
—— —— melting- and solidifying-points of mixed fatty acids from, 197, 314.
—— —— mineral oil in, detection of, 315.
—— —— oxidizability of, comparative, 256.
—— —— oxygen, absorption of, by, 261.
—— —— properties of mixed alcohols from, 221, 224, 233, 234, 315.
—— —— refractive index of, 198.
—— —— refractometer value of, 199, 314.
—— —— Reichert value of, 232.
—— —— saponification value of, 213, 314, 315.
—— —— separation of spermaceti from, 114.
—— —— setting-point of, 191, 314
—— —— Southern and Arctic, comparison of, 313, 314.
—— —— Southern and Arctic, sources of, 114.
—— —— specific gravity of, 176, 314, 315.
—— —— specific gravity of unsaponifiable matter from, 177.
—— —— static coefficient of friction with, 52.
—— —— testing of, for adulterants, 313, 314, 315.
—— —— unsaponifiable matter in, per cent., 223, 314, 315.
—— —— unsaponifiable matter in, properties of, 221, 224, 233, 234, 315.
—— —— unsaponifiable matter in, yield of acetates from, 234.
—— —— viscosity of and effect of temperature on, 114, 115, 159, 160, 314.
Spermaceti, composition of, 233.
—— iodine value of, 245.
—— melting-point of, 196.
—— saponification value of, 213.
—— separation of, from sperm oil, 114.
—— specific gravity of, 176.
—— unsaponifiable matter in, per cent., 223.
Spindle bearing, Parsons', Hon. C. A., 375.
Spindle oils from astatki, 96.
—— —— viscosity of, 159, 160, 298.
Spontaneous combustion of oily rags, etc., 268–272.
—— —— causes of, 268.
—— —— danger of, from free fatty acid in oils, 268.
Spontaneous combustion, influence of the nature of the fibrous material on, 268.
—— —— prevented by mineral oil, 269.
—— —— testing oils to ascertain their liability to, 269–272.
Sprengel-tube for specific gravity determinations, 166, 167.
Spring (Walthère); welding of metallic powders, 4, 5.
Staining of fabrics by lubricants, 398.
Stains, oil, cause and removal of, 399.
Steam-refining process for mineral lubricating oils, 91.
Steinbuch; Reichert-Meissl value of porpoise body and jaw oils, 116, 232.
Stephenson's alloy, 351.
Stock; corrosion of iron by free fatty acids, 206.
—— method of determining melting-point of grease, 193.
—— Milliau test for cottonseed oil, 279.
Storch; colour reaction of rosin oil, 282.
—— estimation of rosin oil in mineral oil, 285.
Straining of lubricants, 404.
Stroudley's oil-testing machine (*drum*), 331.
'Sulphocarbon oil' (refuse olive oil), 106.
Sulphuric acid, free, in refined rape oil, 301.
Sulphuric acid (Maumené) thermal test for oils, 250–254.
Sunflower oil, iodine value of, 245.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197.
—— —— oxidizability of, comparative, 256.
—— —— refractometer value of, 199.
—— —— Reichert-Meissl value of, 232.
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
'Sunned oil,' 92.
'Sunning' process, 92.
Superficial tension and lubrication, 31–48.
—— —— and solubility, 39.
—— —— at interfaces of liquids and solids, 36.
—— —— caused by stresses of surface molecules, 33.
—— —— circumstances which modify, 39.
—— —— effect of, on lubricating films, 53.
—— —— effects of contamination on, 41.
—— —— evaporation related to, 39.
—— —— influence of, on behaviour of liquids in contact, 36.

[illegible] tension, influence of, on mobility of liquids and solids in [illegible].
—— —— in [illegible] surfaces, [illegible].
—— —— of [illegible] surfaces, [illegible].
—— —— of [illegible] surfaces, [illegible].
—— —— measurement of, [illegible].
—— —— measurement of, by [illegible], [illegible].
—— —— measurement of, by [illegible] in [illegible], [illegible].
—— —— measurement of, by [illegible], [illegible].
—— —— measurement of, by vertical plate, [illegible].
—— —— theory of, [illegible].

[illegible] standard of [illegible], [illegible].
Tallow, acetyl value of, [illegible].
—— acid, free, in, [illegible].
—— characters, general, of, [illegible].
—— composition of, [illegible].
—— constants of genuine, [illegible].
—— for grease-making, [illegible].
—— iodine value of, 245, [illegible].
—— iodine value of mixed fatty acids from, 245.
—— lubricant, with graphite, for heavy loads, [illegible].
—— melting-point of, [illegible].
—— melting- and solidifying-points of mixed fatty acids from, [illegible].
—— Reichert and Meissl values of, 232.
—— rendering of, [illegible].
—— saponification value of, [illegible].
—— sources of, [illegible].
—— suspended insoluble impurities in, [illegible].
—— specific gravity of, 176.
—— specific gravity of mixed fatty acids from, 177.
—— testing of, for adulterants, etc., 310, 311.
—— unsaponifiable matter in, per cent., 223.
—— valuation of, by the 'titre test,' 311.
—— viscosity of, 159.
—— water in, 310.
Tallow oil, characters, general, of, 112.
—— —— composition of, 112.
—— —— constants of genuine, 303.
—— —— expression of, from tallow, 112.
—— —— iodine value of, 245, 311.
—— —— lubricant, used for mixing with mineral oil, 101, 112.
—— —— refractometer value of, 199.
—— —— solidifying-point of, 311.
—— —— specific gravity of, 311.
Tallow oil, testing of, 311.
—— —— (see also *Animal oil*).
Tallow 'stearine,' 112.
Tar oil, specific gravity of, 177.
Testing of lubricants, by chemical and physical methods, 295–318.
—— —— by mechanical methods, 319–340.
—— of fixed oils and fats, 300–316.
—— of mineral oils, 296–300.
—— of mixed oils and greases, 317, 318.
—— of undescribed oils, 295.
Testing machines, mechanical, 319–340.
—— —— disc and collar forms, 335–340.
—— —— design of, 320.
—— —— drum form, 322–335.
—— —— nature of tests with, 320.
—— —— purposes used for, 321.
—— —— suitability of disc and collar forms of, 335.
—— —— value of, for testing lubricants, 319.
Thermal test for oils with bromine, 247–250.
—— —— for oils with sulphuric acid, 250–254.
Thickened oils (see *Blown oils*).
Thörner; Reichert-Meissl values of oils, 231.
Thomson: free acid in oils, 203, 204.
—— and Ballantyne, specific temperature reaction, 253.
—— —— changes produced by blowing oils, 117, 316.
Thurston, R. H.: experiments on static friction, 52.
—— the selection of economical lubricants, 426.
Thurston's oil-testing machine (*drum*), design of, 322.
—— —— machine, methods of working, 327.
Titre-test, 196.
Tools, lubrication of cutting-, 422.
Tortelli and Ruggeri; estimation of arachis oil in olive oil, 274–276.
Tower (Beauchamp), experiments on lubrication, 31.
—— —— experiments on pivot friction, 64.
—— —— friction experiments (*reference*), 50.
—— —— on collar-bearings, 380.
—— —— on pivot-bearings, 381.
—— —— on positions for oil-ways of bearings, 360.
—— —— testing-machine (*collar*), 339.
—— —— testing-machine (*disc or pivot*), 339.
—— —— testing-machine (*drum*), 333.

Tower (Beauchamp), viscosity and cylindrical bearing friction, 78.
—— —— wear of bearings, 368.
Train oil, comparative oxidizability of, 256.
Tram-cars, viscosity of oils for, 298.
Trimmings, examination of, 415.
—— flow of lubricants in, 43.
Turner's sclerometer, 346.
Twitchell; process for estimation of rosin (colophony), 227-229.

Ulzer (see *Benedikt*).
Unsaponifiable matter, composition and identification of, 219-224.
—— —— determination of, 215-219.
—— —— examination of, by acetylation process, 231-235.
—— —— from sperm oil and solid waxes, 224.
—— —— identification of hydrocarbons in, 219.
—— —— identification of wax alcohols in, 221.
—— —— identification of cholesterols in, 222.
—— —— soap in the, 223.
—— —— unsaponifiable oil in, 223.
—— —— use of determining the, 215.
Unwin; 'carboid' for bearings, 354.
—— on estimation of hardness, 345.

Vacuum process of distillation, 91.
Valenta; characteristics of bone fat, 311.
'Valvoline,' cylinder oil, viscosity of, 159, 161.
Van Leent; refractometer values of oils, 199.
Vaseline, identification of, in unsaponifiable matter, 220.
—— iodine value of, 246.
—— lubricant, with graphite, for heavy loads, 405.
—— melting-point of, 196.
—— obtained from petroleum, 90.
—— saponification value of (*nil*), 213.
—— specific gravity of, 176, 220.
Vegetable oils, distinction of, from animal oils, 222.
—— used for lubrication, list of, 101.
—— (see *Fixed oils*).
Villavecchia and Fabris; furfurol test for sesamé oil, 281.
—— —— observations on olive oil, 281.
Vince; friction research, 6.
Virgin (olive) oil, 106.
'Viscom,' for thickening mineral oils, 120, 291.
Viscometer, absolute, description of an, 127-129.
Viscometer, Coleman-Archbutt, 140-143.
—— Engler's standard, 144-145.
—— inlet end resistance of capillary tube of, 28.
—— Kunkler's, 145-147.
—— method of standardizing a commercial, 148-153.
—— proportions of, 28.
—— Redwood's standard, 138-140.
—— results obtained by standardizing Redwood's and Coleman's, 149-153.
—— Saybolt's, 143-144.
—— standardized commercial, rules for determining viscosity by means of, 153.
Viscometry, absolute, 126-137.
—— commercial, 137-153.
—— Poiseuille's absolute method of, 126.
—— rules for, by means of standardized commercial viscometer, 153.
Viscosity, absolute, of oils determined by the Coleman viscometer, 154-157.
—— absolute, of oils determined by the Redwood viscometer, 158.
—— absolute, summary of determinations, 159.
—— cohesion and, 17.
—— critical velocity of liquids and, 24.
—— determination of (see *Viscometry*).
—— direct viscous flow and, 23.
—— effects of, on friction of bearings, 76, 355, 358.
—— effects of temperature and pressure on, 25.
—— energy-correction in estimating, 27.
—— expression of, 19, 140, 145, 147.
—— factitious, 120.
—— heating of bearings produced by, 417.
—— liquid, 16-29.
—— mechanical, 23.
—— nature of, 16.
—— of castor oil, 159, 161.
—— of glycerol and water, determination of, 130-134.
—— of glycerol and water, table of, 134-137.
—— of lubricants causes friction, 397.
—— of oils for different purposes, 298.
—— of oils, precautions in determining, 139.
—— of olive oil, 159-160.
—— of mineral lubricating oils, 97, 159, 160, 161.
—— of rape oil, 159, 161.
—— of tallow, 159.
—— of water, determination of, 129, 130.
—— physical, 23.
—— sources of error in determining, 27.
Viscous flow, circumstances which conduce to steady, 26.

[illegible] flow, conditions determining steady, [illegible].
—— —— between parallel planes having differential motion, [illegible].
—— —— by gravity between fixed planes, [illegible].
—— —— through capillary tubes, 22.
Volatile fatty acids, estimation of, [illegible].
Volatility and flashing-points compared, [illegible].
Volatility, determination of, [illegible].
—— of mineral cylinder oils, [illegible].
—— of mineral lubricating oils, [illegible].
[illegible] lining alloy for bearings, 351.

[illegible], R. : on acetyl values of oxidised oils, [illegible].
—— on Benedikt's acetyl values, [illegible].
[illegible]; determination of the iodine value of oils, [illegible].
Walnut oil, acetyl value of, [illegible].
—— —— iodine value of, [illegible].
—— —— iodine value of mixed fatty acids from, [illegible].
—— —— melting- and solidifying-points of mixed fatty acids from, [illegible].
—— —— oxidation of, increase of weight during, [illegible], [illegible].
—— —— refractive index of, [illegible].
—— —— refractometer value of, [illegible].
—— —— saponification value of, 213.
—— —— setting-point of, 191.
—— —— specific gravity of, 176.
Wartha; corrosive action of oleic acid upon iron, 206.
Watch-glass test for oxidizing property of oils, 255.
Watch-oil, Kelley's, results of examination of, 116.
Water, detection and estimation of, in oils and greases, 293, 294.
—— density of, at 4°-100° C. (*table*), 174.
—— viscosity of, at 20° C., 129, 130.
Waxes, composition of, 100.
—— distinction of, from fats and oils, 100.
—— estimation of unsaponifiable matter in, 215.
—— iodine values of (*table*), 245.
—— melting-points of (*table*), 196.
—— properties of mixed alcohols obtained from (*table*), 224.
—— results obtained by acetylation of mixed alcohols from, 234.
—— saponification values of, 213.
—— specific gravities at 60° F. of, 176.
—— unsaponifiable matter in, per cent., 223.
Wear, estimation of losses due to, 426.
—— of cylindrical bearings, 81
Wear of surfaces, 3.
Wellington; on friction of railway vehicles, 60.
Westinghouse; experiments on brake friction, 11.
Westphal balance (hydrostatic), for determining specific gravity, 167-[illegible].
Wetting of solids by liquids, [illegible].
—— liquids, theory of, 42.
Whale oil, acid, free, in, 313.
—— —— characters of, as lubricant, 114.
—— —— characters of refined, 312.
—— —— constants of genuine, 308.
—— —— distinction of, from sperm oil, 112.
—— —— iodine value of, 245, 312.
—— —— iodine value of mixed fatty acids from, 245.
—— —— melting- and solidifying-points of mixed fatty acids from, 197, 312.
—— —— oxidisability of, comparative, [illegible].
—— —— refractive index of, 198.
—— —— refractometer value of, 199, 312.
—— —— Reichert value of, 232.
—— —— saponification value of, 213.
—— —— sources of, 112.
—— —— specific gravity of, 176, 312.
—— —— specific gravity of mixed fatty acids from, 177.
—— —— testing of, 313.
—— —— unsaponifiable matter in, per cent., 223.
—— —— use of, as lubricant, 101, 114.
White-metals for bearings, 351.
Whitworth; on the adhesion of metals, 4.
Wicks, flow of lubricants through, 43.
Wijs's iodine values compared with Hübl values, 244.
—— process for determining the iodine value, 244.
—— reactions occurring in Hübl's iodine process, 241, 243-247.
Wilberforce; correction for kinetic energy (*viscometry*), 27, 130.
Wiley; Milliau test for cottonseed oil, 279.
Wilhelmey; measurement of superficial tension, 47.
Williams (Rowland); iodine value of tallow, 310.
—— Milliau test for cottonseed oil, 279.
Wilson, J. A.; average (*Benedikt*) acetyl values of oils, 238.
Wilson, J. Veitch; acid, free, in sperm and whale oils, 204, 313.
—— —— blown oils as lubricants, 119.
—— —— characters of blown oils, 117, 118.
—— —— flashing-point of sperm oil, 315.

Wilson, J. Veitch; flashing-points and volatility of oils, 178, 183.
—— —— temperature and time of blowing oils, 117.
—— —— oiliness of lubricants, 31.
—— —— volatility of oils, 183.
Wolff, C. E. (and Deeley); on lubrication of plain parallel surfaces, 64.
Wood for bearings, 353.
Woodbury's mechanical oil-testing machine (*disc*), 337.
Wool-fat, characteristics and identification of mixed alcohols from, 221, 224, 233, 234.
—— estimation of, in presence of mineral oil, 233.
—— estimation of unsaponifiable matter in, 217.
—— iodine value of, 245.
—— iodine value of mixed alcohols from, 246.
Wool-fat, melting-point of, 196.
—— melting- and solidifying-points of mixed fatty acids from, 197.
—— Reichert-Meissl value of, 232.
—— saponification value of, 213.
—— specific gravity of, 176.
—— specific gravity of mixed alcohols from, 177.
—— unsaponifiable matter in, per cent., 223.
Wright, Alder; iodine value of tallow, 310.
—— reduction of specific gravity to a vacuum, 172.

YOUNG, Dr Thos.; on molecular adhesion, 17.
—— Dr Jas.; spontaneous ignition of oily rags, etc., 268.

ERRATA.

Page 45,	line 11 from top,	for *Rucker*	read *Rücker*.
,, 288	,, 8 from bottom,	,, *benzine*	,, *benzene*.
,, 315	,, 18 from top,	,, *Lobey*	,, *Lobry*.
,, 351	,, 5 from bottom of table,	,, *Voncher*	,, *Vaucher*.

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